(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 March 2006 (23.03.2006)

PCT

(10) International Publication Number
WO 2006/031358 A2

(51) International Patent Classification:
A61K 31/785 (2006.01)

(21) International Application Number: PCT/US2005/029097

(22) International Filing Date: 15 August 2005 (15.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/601691 13 August 2004 (13.08.2004) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/031358 A2

(54) **Title:** DENDRITIC POLYMERS, CROSSLINKED GELS, AND THEIR USES AS OPHTHALMIC SEALANTS AND LENSES

(57) **Abstract:** The present invention provides compositions and methods for sealing a wound and preparing a lens. The methods of the invention utilize dendritic macromolecules formed by treating a dendritic compound with light or a linking compound. In certain instances, the dendritic compounds have a lysine-, cysteine-, isocysteine-residue or other nucleophilic group attached to the periphery of the dendrimer: Addition of a compound containing two or more electrophilic groups such as aldehydes, activated esters, or acrylates to the lysine-, cysteine-, or isocysteine-capped dendrimers produces a polymeric compound that can form a seal or a lens. Another aspect of the invention relates to a method of treating disease using the pharmaceutical compositions of the invention. Other aspects of the invention relate to kits for sealing a wound or preparing a lens, delivery devices, and methods for controlling the polymerization of a hydrogel system.

Dendritic Polymers, Crosslinked Gels, and Their Uses as Ophthalmic Sealants and Lenses

Related Applications

This application claims the benefit of priority to United States Provisional Patent Application serial number 60/601,691, filed August 13, 2004, which is incorporated by reference.

Background of the Invention

Ophthalmic sealants and adhesives play an important role in helping patients recover from eye surgery or eye trauma. Ophthalmic sealants and adhesives are useful in treating patients suffering from a variety of ophthalmic conditions, including corneal lacerations, retinal tears, corneal transplants, and cataract procedures. These dendritic polymers and crosslinked gels are also useful as a lens replacement material, a lens substitute material, and an intaocular lens. A discussion of each of these conditions is presented below.

Cornea - Corneal Lacerations/Perforations

Corneal perforations are produced by a variety of medical conditions (e.g., infection, inflammation, xerosis, neurotrophication, and degeneration) and traumas (chemical, thermal, surgical, and penetrating). Unfortunately, corneal perforations often lead to loss of vision and a decrease in an individual's quality of life. Depending on the type and the origin of the perforation, different treatments are currently available from suturing the wound to a cornea graft. However, the surgical procedures are difficult given the delicate composition of the cornea and the severity of the wound which increase the likelihood for leakage and severe astigmatism after surgery. In certain cases, perforations that cannot be treated by standard suture procedures, tissue adhesives (glues) are used to repair the wound. This type of treatment is very attractive because the method is simple, quick and safe, and corresponds to the requirement of a quick restoration of the integrity of the globe, avoiding further complications. Besides an easy and fast application on the wound, the criteria for an adhesive are to: 1) bind to the tissue (necrosed or not, very often

wet) with an adequate adhesion force; 2) be non-toxic; 3) be biodegradable or resorbable; 4) be sterilizable; and 5) not interfere with the healing process.

Various alkyl-cyanoacrylates are available for the repair of small perforations. However, these “super glues” present major inconveniences. Their monomers, in particular those with short alkyl chains, can be toxic with formation of formaldehyde. They also polymerize too quickly leading to applications that might be difficult and, once polymerized, the surface of the glue is rough and hard which leads to patient discomfort and a need to wear contact lens. Even though cyanoacrylate is tolerated as a corneal sealant, a number of complications have been reported including cataract formation, corneal infiltration, glaucoma, giant papillary conjunctivitis, and symblepharon formation. Furthermore, in more than 60% of the patients, additional surgical intervention is needed.

Other glues have also been developed. Adhesive hemostats, based on fibrin, are usually constituted of fibrinogen, thrombin and factor XIII. Systems with fibrinogen and photosensitizers activated with light are also being tested. If adhesive hemostats have intrinsic properties which meet the requirements for a tissue adhesive, autologous products (time consuming in an emergency) or severe treatments before clinical use are needed to avoid any contamination to the patient. An ideal sealant for corneal perforations should 1) not impair normal vision, 2) quickly restore the intraocular pressure, IOP, 3) maintain the structural integrity of the eye, 4) promote healing, 5) adhere to moist tissue surfaces, 6) possess solute diffusion properties which are molecular weight dependent and favorable for normal cornea function, 7) possess rheological properties that allow for controlled placement of the polymer on the wound, and 8) polymerize under mild conditions.

The use of sutures has limitations and drawbacks. First, suture placement itself inflicts trauma to corneal tissues, especially when multiple passes are needed. Secondly, although suture material has improved, sutures such as 10-0 nylon (which is the suture of choice in the cornea as well as other in vivo area) can act as a nidus for infection and incite corneal inflammation and vascularization. With persistent inflammation and vascularization, the propensity for corneal scarring increases. Thirdly, corneal suturing often yields uneven healing and resultant regular and irregular astigmatism. Postoperatively, sutures are also prone to becoming loose and/or broken and require additional attention for prompt removal. Finally, effective suturing necessitates an acquired

technical skill that can vary widely from surgeon to surgeon and can also involve prolonged operative time.

Cornea - Corneal Transplants

During a corneal transplant or penetrating keratoplasty surgery the diseased cornea is removed with a special round cutting tool called a trephine. The donor cornea is cut to a matching size. Then, the donor cornea is placed upon the eye and secured in place with approximately 16 sutures around the transplant to secure the new cornea in place. A sutureless procedure would therefore be highly desirable and would offer the following advantages: (1) sutures provide a site for infection, (2) the sutured cornea takes 3 months to heal before the sutures need to be removed, and (3) the strain applied to the new cornea tissue from the sutures can distort the cornea. An ocular adhesive may also serve as an adjuvant to sutures and/or reduce the necessary number of sutures.

Cornea – Clear Corneal Incision

Clear corneal incisions in the temporal cornea offer several advantages with phacoemulsification. The major advantage associated with phacoemulsification is the reduction in size of the entrance wound. Smaller wounds require fewer sutures or even no sutures at all, minimizing induction of astigmatism, decreasing bleeding and subconjunctival hemorrhage, and speeding the recovery of visual acuity. See Agapitos, P. J. *Curr. Opin. Ophthalmol.* **1993**, *4*, 39–43 and Lyle, W. A.; Jin, G. J. *J. Cataract Refract. Surg.* **1996**, *22*, 1456–1460. Surgeons typically examine the clear corneal incisions at the completion of the procedure by inflating the anterior chamber with balanced salt solution and applying pressure to the anterior cornea to check for leakage from the wound. If there is some leakage, the wound may be hydrated with balanced saline solution to fully seal the wound. This is done by injecting balanced saline solution into the open stromal edges. Hydration forces the two edges of the wound together, creating a tight seal. The endothelial cell pump can then remove the fluid from both the anterior and posterior portions of the wound, further sealing the wound together. See Fine, I. H. *J. Cataract Refract. Surg.* **1991**, *17 (Suppl)*, 672-676. These tests for fluid flow, however, make several assumptions, including that the eye will remain well pressurized during the early postoperative period, that the hydrated wound will not be rapidly deturgesced by the corneal endothelium, and that the absence of aqueous outflow from the wound correlates with the inability of surface fluid from the tear film to flow into the wound, possibly contaminating the aqueous humor

and predisposing to infection. However, intraocular pressure is known to vary in the postoperative period, frequently dropping to less than 5 mmHg, and telemetric intraocular pressure monitoring devices suggest that large fluctuations in intraocular pressure occur in individual eyes in response to blinking. See Shingleton, B. J.; Wadhwani, R. A.; O'Donoghue, M. W.; Baylus, S.; Hoey, H. *J. Cataract Refract. Surg.* **2001**, *27*, 524-527 and Percicot, C. L.; Schnell, C. R.; Debon, C.; Hariton, C. *J. Pharmacol. Toxicol. Methods* **1996**, *36*, 223-228.

In a recent study, optical coherence tomography (OCT) confirmed the morphology of clear corneal incision wounds was not constant but varied in response to changes in the intraocular pressure. See McDonnell, P. J.; Taban, M.; Sarayba, M.; Rao, B.; Zhang, J.; Schiffman, R.; Chen, Z. P. *Ophthalmology* **2003**, *110*, 2342-2348. When the eyes were well pressurized (20 mmHg or higher), the chambers were deeply formed, and the wound edges were well apposed. Elevation of intraocular pressure up to 40 to 50 mmHg did not result in any separation of the wound edges. As the intraocular pressure was reduced to 10 mm Hg and below, the wound edges progressively separated. The separation began at the internal aspect of the wound, with posterior migration of the posterior and peripheral wound leaflet. This separation resulted in a wedge-shaped gaping in the internal aspect of the incision. Coincident with this wound margin separation, the spontaneous flow of aqueous through the wound was observed, and the chamber became shallower. Elevating the intraocular pressure resulted in prompt closure of the corneal wound at its superficial margin, termination of fluid leakage from the wound, and deepening of the anterior chamber. India ink was also applied to the surface of the cornea and quickly became visible through the operating microscope within the clear corneal incisions. Histologic examination of the wounds confirmed partial penetration of India ink particles along the edges of the incisions in every cornea. These studies demonstrated that a transient reduction of intraocular pressure might result in poor wound apposition in clear corneal incisions, with the potential for fluid flow across the cornea and into the anterior chamber, with the attendant risk of endophthalmitis. See McDonnell, P. J.; Taban, M.; Sarayba, M.; Rao, B.; Zhang, J.; Schiffman, R.; Chen, Z. P. *Ophthalmology* **2003**, *110*, 2342-2348.

Nonetheless, a progressive increase in the percentage of surgeons preferring self-sealing clear corneal incisions over scleral tunnel incisions in the United States and Europe has occurred over the past decade. See Leaming, D. V. *J. Cataract Refract. Surg.* **1995**, *21*, 378-385 and Leaming, D. V. *J. Cataract Refract. Surg.* **2001**, *27*, 948–955. Some studies,

however, reveal an increased incidence of postoperative endophthalmitis after clear corneal cataract incisions and a recent, retrospective, case-controlled study, reported that clear corneal incisions were a statistically significant risk factor for acute post-cataract surgery endophthalmitis when compared with scleral tunnel incisions. See John, M. E.; Noblitt, R. *Endophthalmitis. Scleral tunnel vs. clear corneal incision*; Slack, Inc.: Thorofare, NJ, 2001; Colleaux, K. M.; Hamilton, W. K. *Can. J. Ophthalmol.* **2000**, *35*, 373-378; Nagaki, Y.; Hayasaka, S.; Kadoi, C.; Matsumoto, M.; Yanagisawa, S.; Watanabe, K.; Watanabe, K.; Hayasaka, Y.; Ikeda, N.; Sato, S.; Kataoka, Y.; Togashi, M.; Abe, T. *J. Cataract. Refract. Surg.* **2003**, *29*, 20-26; Stonecipher, K. G.; Parmley, V. C.; Jensen, H.; Rowsey, J. J. *Arch. Ophthalmol.* **1991**, *109*, 1562-1563; Lertsumitkul, S.; Myers, P. C.; O'Rourke, M. T.; Chandra, J. *Clin. Exp. Ophthalmol.* **2001**, *29*, 400-405; and Blake, A. C.; Holekamp, N. M.; Bohigian, G.; Thompson, P. A. *Am. J. Ophthalmol.* **2003**, *136*, 300-305. The visual outcome following severe endophthalmitis is always guarded. In a Western Australian Endophthalmitis Study more than half of the subjects suffered visual impairment, with 41% poorer than 20/200, 53% poorer than 20/125, and 58% poorer than 20/40. See Semmens, J. B.; Li, J.; Morlet, N.; Ng, J. *Clin. Exp. Ophthalmol.* **2003**, *31*, 213-219. Post-cataract endophthalmitis remains a potentially blinding complication of a sight-restoring procedure.

Refractive Surgery - Laser-assisted in situ Keratomileusis (LASIK)

Laser-assisted in situ keratomileusis is the popular refractive surgical procedure where a thin, hinged corneal flap is created by a microkeratome blade. This flap is then moved aside to allow an excimer laser beam to ablate the corneal stromal tissue with extreme precision for the correction of myopia (near-sightedness) and astigmatism. At the conclusion of the procedure, the flap is then repositioned and allowed to heal. However, with trauma, this flap can become dislocated prior to healing, resulting in flap striae (folds) and severe visual loss. When this complication occurs, treatment involves prompt replacement of the flap and flap suturing. The use of sutures has limitations and drawbacks as discussed above. These novel adhesives could also play a useful role in the treatment of LASIK flap dislocations and striae (folds). These visually debilitating flap complications are seen not uncommonly following the popular procedure LASIK, and are currently treated by flap repositioning and suturing (which require considerable operative time and technical skill). A tissue adhesive could provide a more effective means to secure the flap.

Refractive surgery – Lens Replacement

Cataracts or other diseases or injuires that lead to poorly functioning or damaged lens require the natural lens to be replaced. The optical properties of the normal eye lens are the consequence of a high concentration of proteins called "crystallins" forming a natural hydrogel. In vertebrate lenses, a range of differently sized protein assemblies, the *alpha -, beta - and gamma*-crystallins, are found creating a medium of high refractive index. The anatomical basis of accommodation includes the lens substance, lens capsule, zonular fibers, ciliary muscle and the elastic part of the choroid. Accommodation occurs through accurately controlled adjustments in the shape and thickness of the lens. The capsular bag is essential in transmitting the various extralenticular forces to the lens substance.

Modern cataract surgery can be done through a small incision (usually 2.5-3.5 mm). Once the incision is made, the anterior chamber is filled with a viscoelastic and the capsular bag is pricked with a needle. From this incision, a small continuous circular capsulorhexis (CCC) approximately 1.5 mm in diameter is performed using capsulorhexis forceps. Next endocapsular phacoemulsification is performed and the lens epithelial cells are removed by aspiration.

http://depts.washington.edu/ophthweb/foldedIOLpic.html The normal function of the lens is to focus light onto the retina. Since removing the cataract leaves the eye without a lens to focus light, an artificial (intraocular) lens is commonly placed inside the eye. Most intraocular lenses are made of plastic, silicone, or acrylic compounds; have no moving parts; and last for the remainder of a person's life. These intraocular lens implants are held in place by the posterior capsule are not able to provide ocular accommodation. **http://depts.washington.edu/ophthweb/unfoldedIOLpic.htmlhttp://depts.washington.edu/ophthweb/capsulotpic.html**Refilling the lens capsule with *in situ* crosslinking materials described herein offers the potential to produce a synthetic hydrogel with mechanical properties similar to the lens of a twenty year old.

As such, the invention describes materials that reproduce the properties of the natural lens and these synthetic hydrogels maintain the integrity of the capsule to gain partial or full accommodation and restore vision to the patient. Alternatively, the dendritic polymers of said invention are incorporated in current IOL materials such as PMMA to alter hydrophilicity, water transport, refractive index, mechanical properties or biological response.

Retina - Retinal Holes

Techniques commonly used for the treatment of retinal holes such as cryotherapy, diathermy and photocoagulation are unsuccessful in the case of complicated retinal detachment, mainly because of the delay in the application and the weak strength of the chorioretinal adhesion. Cyanoacrylate retinopexy has been used in special cases. It has also been demonstrated that the chorioretinal adhesion is stronger and lasts longer than the earlier techniques. As noted previously with regard to corneal perforation treatment, the extremely rapid polymerization of cyanoacrylate glues (for example, risk of adhesion of the injector to the retina), the difficulty to use them in aqueous conditions and the toxicity are inconveniences and risks associated with this method. The polymerization can be slowed down by adding iophendylate to the monomers but still the reaction occurs in two to three seconds. Risks of retinal tear at the edge of the treated hole can also be observed because of the hardness of cyanoacrylate once polymerized.

Retina – Vitrectomy/Sclerotomy Incisions

The vitreous is a normally clear, gel-like substance that fills the center of the eye. It makes up approximately 2/3 of the eye's volume, giving it form and shape before birth. Certain problems affecting the back of the eye may require a vitrectomy, or surgical removal of the vitreous. During a vitrectomy, the surgeon creates small incisions/punctures in the eye (sclerotomies) for separate instruments. These incisions are placed in the pars plana of the eye, which is located just behind the iris but in front of the retina. The instruments which pass through these incisions include a light pipe, an infusion port, and the vitrectomy cutting device. Upon completion of pars plana vitrectomy, each sclerotomy site is closed with a single interrupted suture of 8-0 silk or 7-0 polyglycolic acid suture. After a vitrectomy, the eye is filled with fluid until the vitreous is replaced as the eye secretes aqueous and nutritive fluids.

Some of the most common eye conditions that require vitrectomy include 1) complications from diabetic retinopathy such as retinal detachment or bleeding, 2) macular hole 3) retinal detachment, 4) pre-retinal membrane fibrosis, 5) bleeding inside the eye (vitreous hemorrhage), 6) injury or infection, or 7) certain problems related to previous eye surgery.

Glaucoma - Leaking Bleb

Leaking filtering blebs after glaucoma surgery are difficult to manage and can lead to serious, vision-threatening complications. Leaking blebs can result in hypotony and shallowing of the anterior chamber, choroidal effusion, maculopathy, retinal, and choroidal folds, suprachoroidal hemorrhage, corneal decompensation, peripheral anterior synechiae, and cataract formation. A leaking bleb can also lead to the loss of bleb function and to the severe complications of endophthalmaitis. The incidence of bleb leaks increases with the use of antimetabolites. Bleb leaks in eyes treated with 5-fluorouracil or mitomycin C may occur in as many as 20 to 40% of patients. Bleb leaks in eyes treated with antimetabolities may be difficult to heal because of thin avascular tissue and because of abnormal fibrovascular response. If the leak persists despite the use of conservative management, a 9-0 to 10-0 nylon or absorbable suture on a tapered vascular needle can be used to close the conjunctival wound. In a thin-walled or avascular bleb, a suture may not be advisable because it could tear the tissue and cause a larger leak. Fibrin adhesives have been used to close bleb leaks. The adhesive is applied to conjunctival wound simultaneously with thrombin to form a fibrin clot at the application site. The operative field must be dry during the application because fibrin will not adhere to wet tissue. Cyanoacrylate glue may be used to close a conjuctival opening. To apply the glue, the surrounding tissue must be dried and a single drop of the cyanoacrylate is placed. The operative must be careful not to seal the applicator to the tissue or to seal surrounding tissue with glue given its quick reaction. A soft contact lens is then applied over the glue to decrease patient discomfort. However this procedure can actually worsen the problem if the cyanoacrylate tears from the bleb and causes a larger wound.

Oculoplastics – Blepharoplasty Incisions

Blepharoplasty is an operation to remove excess skin, fat and muscle from around the eyes to correct droopy eyelids and bagginess under the eyes. It can be performed on the upper lids and lower lids, at the same time or separately. The operation may be done using either conventional or laser techniques. For surgery on the upper eyelids, cuts are made into the natural lines and creases in the lid, and into the laughter lines at the corner of the eye. For surgery on the lower eyelids, a cut is usually made just below the eyelashes. This means the scars run along the eye's natural folds, concealing them as much as possible. Excess fat, muscle and loose skin are removed, and the cut is closed using sutures . If only fat is being removed, sometimes the cut is made on the inside of the lower eyelid, leaving no visible

scar. A tissue adhesive could provide a more effective means to secure the cuts made during surgery.

Summary of the Invention

The present invention generally relates to methods of sealing a wound or creating a lens. In a preferred embodiment, the wound is an ophthalmic wound. In certain instances, the compositions used to seal the wound comprise a dendrimer. In certain aspects of the invention, the dendritic polymers have an acrylate group attached at the periphery of the dendrimer. Treatment of the acrylate-capped dendritic polymers with ultraviolet radiation causes the dendritic polymers to polymerize forming a seal. In certain instances, the dendritic polymers have a lysine, cysteine, isocysteine residue or other nucleophilic group attached to the periphery of the dendrimer. Addition of a compound containing two or more electrophilic groups such as aldehydes, activated esters, or acrylates to the lysine-, cysteine-, or isocysteine-capped dendrimers produces a polymeric compound that can form a seal. In certain instances, the compositions used to seal the wound comprise a compound that has a polylysine core to which cysteine, isocysteine, or other nucleophilic groups are attached. Addition of a compound containing two or more electrophilic groups such as aldehydes, activated esters, or acrylates to the cysteine- or isocysteine-capped polylysine compounds produces a polymeric compound that can form a seal. Notably, the dendritic polymer may be functionalized with electrophilic groups, and then treated with a compound comprising nucleophilics groups in order to form a sealant.

Another aspect of the invention features a synthetic lens made using the dendritic polymers of the invention. In certain instances, a synthetic lens is formed and used in an ophthalmic procedure. In certain instances, the compositions used to form the lens comprise a dendrimer for replacement or substitution of a natural lens. In certain aspects of the invention, the dendrimer has an acrylate group attached at the periphery of the dendrimer. Treatment of the acrylated-capped dendrimers with ultraviolet radiation causes the dendrimers to polymerize forming a hydrogel lens material. In certain instances, the dendritic polymers have a lysine, cysteine, or isocysteine residue or other nucleophilic group attached to the periphery of the dendrimer. Addition of a compound containing two or more electrophilic groups such as an aldehyde, activated ester, acrylate to the lysine-, cysteine-, or isocysteine-capped dendrimers produces a hydrogel lens material. In certain instances, the compositions used to form the lens comprise a compound that has a polylysine core to which cysteine or isocysteine groups or other nucleophilic groups are attached. Addition of a compound containing an

electrophilic group such as an aldehyde, activated ester, or acrylate to the cysteine- or isocysteinecapped polylysine compounds produces a hydrogel lens material. Notably, the dendritic polymer may be functionalized with electrophilic groups, and then treated with a compound comprising nucleophilics groups in order to form a lens.

Another aspect of the invention relates to pharmaceutical compositions comprising the dendritic macromolecules of the invention. In certain instances, the pharmaceutical compositions comprise a dendritic macromolecule containing a polylysine core. Another aspect of the invention relates to a method of treating disease using the pharmaceutical compositions of the invention. Another aspect of the invention relates to kits for sealing a wound or preparing a lens. Other aspects of the invention relate to delivery devices and methods for controlling the polymerization of a hydrogel system.

Brief Description of Figures

Figure 1 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 2 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 3 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 4 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 5 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 6 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 7 depicts various monomers that can be used to prepare dendrimers used in the invention.

Figure 8 depicts a dendrimer terminated with nucleoside groups amenable to the invention.

Figure 9 depicts dendrimers and compounds useful for making dendrimers amenable to the present invention.

Figure 10 depicts a double-acting, single-barrel syringe.

Figure 11 depicts a double-barrel syringe.

Detailed Description of the Invention

One aspect of the present invention relates to clinical treatments, such as sealing or repairing ophthalimic wounds or incisions created during an ophthalmic surgery. In particularly preferred forms, the present invention is specifically embodied in the use of novel crosslinkable polymers, such as dendritic macromolecules and their *in vitro*, *in vivo*, and *in situ* uses. These biomaterials/polymers are likely to be an effective sealant/glue for other surgical procedures where the site of the wound is not easily accessible or when sutureless surgery is desirable. These biomaterials/polymers are also likely to be an effective synthetic lens material for restoration of vision after a cataract procedure. The polymers, after being crosslinked, can be seeded with cells and then used to repair the damaged ophthalmic tissue. Alternatively, the polymers and cells can be mixed and then injected into the *in vivo* site and crosslinked *in situ* for tissue repair or replacement. The crosslinked polymers provide a three dimensional templates for new cell growth. Crosslinking, such as with a methacrylated functionalized denditic polymer, can be achieved using light or a chemical reaction. An embodiment of this invention is the preparation of crosslinkable biodendritic macromolecules that can undergo a covalent or non-covalent crosslinking reaction to form a three-deminsional crosslinked gel or network, wherein the crosslinking reaction does not involve a single or multi-photon process (i.e., light). The dendritic polymer can be used for the encapsulation of or the covalent attachment of pharmaceutical agents/drugs such as bioactive peptides (e.g., growth factors), antibacterial compositions, antimicrobial compositions, and antinflammatory compounds to aid/enhance the closure and repair of the wound.

Another aspect of the invention is the use of the dendritic polymer to form a synthetic hydrogel lens or lens material. The crosslinkable formulation is injected via a small openinging into an empty lens capsule bag. Subsequent crosslinking by a photochemical or chemical reaction affords a hydrogel lens. Alternatively, these dendritic

polymers can be combined with conventional IOL materials such as acrylates and used in a cataract or other lens removal and replacment procedure. An additional embodiment is the use of the branched structures to increase the refractive index or the incorporation of aromatic amino acids or other aromatic or heterocycles into the dendritic structure to increase the refractive index.

Another aspect of the invention is the use of these dendritic polymers to create a lens whereby a hydrogel gel is afforded that contains one or more additives which increases the refractive index of the gel. These additives may be small or large molecule carbohydrates, amino acids, peptides, or other water soluble polymers (linear or branched), small molecules (e.g., phenol, phe, trp,), natural polymers (e.g., albumin, hyaluronic acid, collagen, alginate, polyglutamic acid, polyamino acids), and/or synthetic polymers (e.g., polymethylmethacrylate, polyacrylic acid, sulfonated-polystyrene, silicone, polyvinyl alcohol). Synthetic aromatic or heterocyclic polymers and polymers having an amide, urea, thiourea, or the like linkages are preferred embodiments. Polymers and small molecules which possess a high refractive index (above 1.10) are specific examples of the additives which may be used in this optical system.

Dendritic Macromolecules

Dendritic polymers are globular monodispersed polymers composed of repeated branching units emitting from a central core. (US5714166; US4289872; US4435548; US5041516; US5362843; US5154853; US05739256; US5602226; US5514764; Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665-1688. Fischer, M.; Vogtle, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 884-905. Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681-1712. Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 138.) These macromolecules are synthesized using either a divergent (from core to surface) (Buhleier, W.; Wehner, F. V.; Vogtle, F. *Synthesis* **1987**, 155-158. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polymer Journal* **1985**, *17*, 117-132. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466. Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003.) or a convergent approach (from surface to core). See Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638-7647. This research area has undergone tremendous growth in the last decade since the early work of Tomalia and Newkome.

Compared to linear polymers, dendrimers are highly ordered, possess high surface area to volume ratios, and exhibit numerous end groups for functionalization. Consequently, dendrimers display several favorable physical properties for both industrial and biomedical applications including: small polydispersity indexes (PDI), low viscosities, high solubility and miscibility, and excellent adhesive properties. The majority of dendrimers investigated for biomedical/biotechnology applications (e.g., MRI, gene delivery, and cancer treatment) are derivatives of aromatic polyether or aliphatic amides and thus are not ideal for *in vivo* uses. (Service, R. F. *Science* **1995**, *267*, 458-459. Lindhorst, T. K.; Kieburg, C. *Angew. Chem. Int. Ed.* **1996**, *35*, 1953-1956. Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Yayaraman, N.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **1997**, *1997*, 732-735. Wiener, E. C.; Brechbeil, M. W.; Brothers, H.; Magin, R. L.; Gansow, O. A.; Tomalia, D. A.; Lauterbur, P. C. *Magn. Reson. Med.* **1994**, *31*, 1-8. Wiener, E. C.; Auteri, F. P.; Chen, J. W.; Brechbeil, M. W.; Gansow, O. A.; Schneider, D. S.; Beldford, R. L.; Clarkson, R. B.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1996**, *118*, 7774-7782. Toth, E.; Pubanz, D.; Vauthey, S.; Helm, L.; Merbach, A. E. *Chem. Eur. J.* **1996**, *2*, 1607-1615. Adam, G. A.; Neuerburg, J.; Spuntrup, E.; Muhl;er, A.; Scherer, K.; Gunther, R. W. *J. Magn. Reson. Imag.* **1994**, *4*, 462-466. Bourne, M. W.; Margerun, L.; Hylton, N.; Campion, B.; Lai, J. J.; Dereugin, N.; Higgins, C. B. *J. Magn. Reson. Imag.* **1996**, *6*, 305-310. Miller, A. D. *Angew. Chem. Int. Ed.* **1998**, *37*, 1768-1785. Kukowska-Latallo, J. F.; Bielinska, A. U.; Johnson, J.; Spinder, R.; Tomalia, D. A.; Baker, J. R. *Proc. Natl. Acad. Sci.* **1996**, *93*, 4897-4902. Hawthorne, M. F. *Angew. Chem. Int. Ed.* **1993**, *32*, 950-984. Qualmann, B.; Kessels M.M.; Musiol H.; Sierralta W.D.; Jungblut P.W.; L., M. *Angew. Chem. Int. Ed.* **1996**, *35*, 909-911). Biodendrimers are a novel class of dendritic macromolecules composed entirely of building blocks known to be biocompatible or degradable to natural metabolites *in vivo*. This patent describes the synthesis, characterization, and use of novel dendrimers and dendritic macromolecules called "biodendrimers or biodendritic macromolecules" composed of such biocompatible or natural metabolite monomers such as but not limited to glycerol, lactic acid, glycolic acid, succinic acid, ribose, adipic acid, malic acid, glucose, citric acid, glycine, lysine, cysteine, alanine, etc. A further embodiment of the invention is a dendritic structure that possess glycerol and one or more of lactic acid, glycolic acid, succinic acid, ribose, adipic acid, malic acid, glucose, citric acid, glycine, lysine, cysteine, alanine, etc. as a building block. In certain instances, the dendrimer is terminated with a photoreactive group or nucleophilic group. In certain instances, the terminus of the dendrimer contains a nucleoside. An

additional embodiment of the invention is a dendritic structure that is composed of all lysine resides such that it is a generation one or higher or a lysine dendritic macromolecule terminated with cystene residues such that it is a generation one or higher.

The present invention is generally in the area of the synthesis and fabrication of dendritic polymers and copolymers of polyesters, polyethers, polyether-esters, and polyamino acids or combinations thereof. For example, linear poly(glycolic acid), poly(lactic acid), and their copolymers are synthetic polyesters that have been approved by the FDA for certain uses, and have been used successfully as sutures, drug delivery carriers, and tissue engineering scaffold for organ failure or tissue loss (Gilding and Reed, Polymer, 20:1459 (1979); Mooney et al., Cell Transpl., 2:203 (1994); and Lewis, D. H. in Biodegradable Polymers as Drug Delivery Systems, Chasin, M., and Langer, R., Eds., Marcel Dekker, New York, 1990). In tissue engineering applications, isolated cells or cell clusters are attached onto or embedded in a synthetic biodegradable polymer scaffold and this polymer-cell scaffold is next implanted into recipients (Langer and Vacanti, Science, 260:920 (1993). A large number of cell types have been used including cartilage cells (Freed et al., Bio/Technology, 12:689 (1994)). Like the novel biodendrimers described in this invention, the advantages include their degradability in the physiological environment to yield naturally occurring metabolic products and the ability to control their rate of degradation by varying the ratio of lactic acid. In the dendritic structures the degradation can be controlled by both the type of monomer used and the generation number.

A further embodiment of this invention is to attach biological recognition units for cell recognition to the end groups or within the dendrimer structure. For example, the tripeptide arginine-glycine-aspartic (RGD), can be added to the structure for cell binding. Barrera et al. described the synthesis of a poly(lactic acid) (pLAL) containing a low concentration of N-epsilon.-carbobenzoxy-L-lysine units. The polymers were chemically modified through reaction of the lysine units to introduce arginine-glycine-aspartic acid peptide sequences or other growth factors to improve polymer-cell interactions (Barrera et al., J. Am. Chem. Soc., 115:11010 (1993); U.S. Pat. No. 5,399,665 to Bartera et al.). The greatest limitation in the copolymers developed by Barrera et al. is that only a limited number of lysine units can be incorporated into the backbone. In many tissue engineering applications, the concentration of biologically active molecules attached to the linear polymer is too low to produce the desired interactions between the polymer and the body. Consequently, there is a need for the development of optimal materials for use as sealants,

adhesives, or temporary scaffolds to support cell growth and tissue development in tissue engineering and wound repair applications. In addition, there is a need for methods for introducing functionalities such as polyamino acids, peptides, carbohydrates into polyesters, polyether-esters, polycarbonates, etc. in order to improve the biocompatibility, biochemical, mechanical, and other properties of the polymers. Furthermore there is a need for the development of polyester, polyether ester, polyester-amines, etc materials which include a sufficient concentration of derivatizable groups to permit the chemical modification of the polymer for different biomedical applications.

It is therefore an object of the invention to provide dendritic polymers and copolymers of polyesters and polyamino acids, polyethers, polyurethanes, polycarbonates, polycarbamates, polyamino alcohols or combinations of these polymer classess which can be chemically modified for different biomedical applications such as tissue engineering applications, wound management, contrast agents vehicles, drug delivery vechiles, etc. It is a further object of the invention to provide dendritic polymers and copolymers of polyesters and polyamino acids with improved properties such as biodegradability, biocompatibility, mechanical strength. It is still another object of the invention to provide dendritic polymers that can be derivatized to include functionalities such as peptide sequences or growth factors to improve the interaction of the polymer with cells, tissues, or bone.

The advantages of a dendritic polymer include multiple end groups for functionalization, crosslinked gels with high crosslinking densities at low polymer concentration, globular structure, low viscosities, and well-defined composition. Conventional linear polymers for medical applications cannot be easily controlled or modified through changes in the polymer's structure, because these polymers (e.g., PLA) do not possess functional groups, other than end groups, that permit chemical modification to change their properties, and these polymers do not adopt a well-defined structure in solution, thereby limiting the applications of these polymers. Consequently the novel polymers described herein are substantially different.

Gels

Another aspect of the present invention relates to using dendritic polymeric gels, gel-cell, gel-drug compositions for ophthalmic surgeries, drug delivery, and tissue

engineering. Gels are 3D polymeric materials which exhibit the ability to swell in water and to retain a fraction of water within the structure without dissolving. The physical properties exhibited by gels such as water content, sensitivity to environmental conditions (*e.g.*, pH, temperature, solvent, stress), soft, adhesivity, and rubbery consistency are favorable for biomedical and biotechnological applications. Indeed, gels may be used as coatings (*e.g.* biosensors, catheters, and sutures), as "homogeneous" materials (*e.g.* contact lenses, burn dressings, and dentures), and as devices (*e.g.* artificial organs and drug delivery systems) (Peppas, N. A. *Hydrogel in Medicine and Pharmacy, Vol I and II* **1987**. Wichterle, O.; Lim, D. *Nature* **1960**, *185*, 117-118. Ottenbrite, R. M.; Huang, S. J.; Park, K. *Hydrogels and Biodegradable polymers for Bioapplications* **1994**; Vol. 627, pp 268).

For example, gel matrices for the entrapment of cells, including stem cells, as artificial organs/tissues have been explored for more than fifteen years in some applications, and encapsulation is a promising approach for a number of disease states including Parkinson's disease (L-dopamine cells), liver disease (hepatocyte cells), and diabetes (islets of Langerhans). In the past, for example, islets of Langerhans (the insulin producing cells of the pancreas) have embedded encapsulated in an ionically crosslinked alginate (a natural hydrogel) microcapsule with a poly-L-lysine coating, and successfully reduced blood sugar levels in diabetic mice following transplantation. With regards to this invention the entrapment of cells in the gel to create a artificial cornea to replace or aid in the repair of a damaged cornea.

Another aspect of the present invention relates to a method and means for designing, constructing, and utilizing artificial dendritic matrices as temporary scaffolding for cellular growth and implantation. A further embodiment of the invention to provide biodegradable, non-toxic matrices which can be utilized for cell growth, both *in vitro*, *in vivo*, and *in situ*. The cell scaffold/matrix/gel can be formed *in vitro* or *in situ* by crosslinking. It is another object of the present invention to provide a method for configuring and constructing biodegradable artificial matrices such that they not only provide a support for cell growth but allow and enhance vascularization and differentiation of the growing cell mass following implantation. It is yet another object of the invention to provide matrices in different configurations so that cell behavior and interaction with other cells, cell substrates, and molecular signals can be studied *in vitro*.

Ophthalmic Sealants/Adhesives

The dendritic macromolecules of the present invention are usefully employed as a general tissue sealant or adhesive. A further embodiment of this invention is the composition and use of these polymers as an ophthalmic sealant or adhesive for corneal lacerations, retinal tears, corneal transplants, and catatact procedures. This is by no means a complete list of examples, but is only to show some representative examples where this material can be used and those skilled in the art will reconginze that the sealant/adhesive has wide-spread application in ophthalmic and general surgeries. A further embodiment of this invention is to use biodendritic crosslinkable polymers for sealing corneal perforations. A further embodiment of this invention is to use biodendritic crosslinkable polymer for sealing retinal holes. A further embodiment of this invention is to use biodendritic crosslinkable polymers for sealing leaking blebs. A further embodiment of this invention is to use biodendritic crosslinkable polymers for sealing a corneal transplant.

Besides ophthalmological applications these crosslinkable polymers have additional surgical uses when the site of the wound is not easily accessible or when sutureless surgery is desired. These crosslinkable sealants/glues may be of potential use for cardiovascular surgery (aortic dissection, anastomotic bleeding), urinary tract surgery (nephrotomy closure, urethral repair, hypospadia repair), pulmonary surgery (sealing parenchymal & bronchial leaks, bronchopleural fistula repair, persistent air leak repairs), G.I. tract and stomach surgery (parotid cutaneous fistula, tracheo-oesophageal fistula, peptic ulcer repair), joint surgery (cartilage repair, meniscal repair), heart surgery (cardiac ventricular rupture repair), brain surgery (dural defect repairs), ear surgery (ear drum perforation), and post-surgical drainage reduction (mastectomy, axillary dissection). The ease of application, as well as the ability to quickly and precisely seal a wet or dry wound, means that this material may prove to be superior to the previous glues used in many of the above application.

Biologically Active Agents Within the Dendritic Gel/Network

In certain instances, biologically active agents may be incorporated in the dendritic gel. Active agents amenable for use in the compositions of the present invention include growth factors, such as transforming growth factors (TGFs), fibroblast growth factors (FGFs), platelet derived growth factors (PDGFs), epidermal growth factors (EGFs), connective tissue ctivated peptides (CTAPs), osteogenic factors, and biologically active

analogs, fragments, and derivatives of such growth factors. Members of the transforming growth factor (TGF) supergene family, which are multifunctional regulatory proteins, are particularly preferred. Members of the TGF supergene family include the beta transforming growth factors (for example, TGF-β1, TGF-β2, TGF-β3); bone morphogenetic proteins (for example, BMP-1, BMP-2, BMP-3, BMP-4, BMP-5, BMP-6, BMP-7, BMP-8, BMP-9); heparin-binding growth factors (for example, fibroblast growth factor (FGF), epidermal growth factor (EGF), platelet-derived growth factor (PDGF), insulin-like growth factor (IGF)); Inhibins (for example, Inhibin A, Inhibin B); growth differentiating factors (for example, GDF- 1); and Activins (for example, Activin A, Activin B, Activin AB).

Wound dressings

In many respects these biomaterials are also of use as a wound dressing. In the majority of the cases, the treatment used for wound closure is the classical suture technique. However, depending on the type, the origin of the wound as well as the location of the patient, the use of tissue adhesives (e.g., glues, sealants, patches, films and the like is an attractive alternative to the use of sutures. Beside an easy and fast application on the wound, the general criteria for an adhesive are to bind to the tissue (necrosed or not, sometimes wet) with an adequate adhesion force, to be non-toxic, biodegradable or resorbable, sterilizable, selectively permeable to gases, impermeable to bacteria and able to control evaporative water loss. Finally, the two main properties of the adhesive are to protect the wound and to enhance the healing process, or at least not prevent it. Numerous sealants have been investigated and used for different clinical applications.

Adhesive hemostats, based on fibrin, are the most common products of biological origin. These sealants are usually constituted of fibrinogen, thrombin and factor XIII, as well as fibrinogen/photosensitizers systems. If their intrinsic properties meet the requirements for a tissue adhesive, autologous products (which are time consuming in emergency) or severe treatments before clinical use are needed to avoid any contamination to the patient.

Synthetic materials, mainly polymers and hydrogels in particular have been developed for wound closure. Alkyl-cyanoacrylates are available for the repair of cornea perforations. One investigator has observed no difference in healed skin incisions that were treated by suture or by ethyl-2-cyanoacrylate-“Mediglue” application. However, these

"super glues" present major inconveniences. Their monomers, in particular those with short alkyl chains, are or might be toxic and they polymerize too quickly leading to difficulty in treating the wound. Once polymerized, the surface of the glue is rough and hard. This might involve discomfort to the patient and, for example, in case of cornea perforation treatment, a contact lens needs to be worn. Other materials have been commercialized such as "Biobrane II" (composite of polydimethylsiloxane on nylon fabric) and "Opsite" (polyurethane layer with vinyl ether coating on one side). A new polymeric hemostat (poly-N-acetyl glucosamine) has been studied for biomedical applications such as treatment of gastric varices in order to replace cyanoacrylate (vournakis). Adhesives based on modified gelatin are also found to treat skin wounds. Photopolymerizable poly(ethylene glycol) substituted with lactate and acrylate groups are used to seal air leaks in lung surgery.

Crosslinked Gels or Networks

To prepare the dendritic crosslinked gel/network of the present invention, dendrimers or dendritic polymers are crosslinked using either light or a chemical crosslinking reaction-non light activated. A large number of crosslinking reactions are amenable to the present invention. For example, the crosslinking reaction may be an acyrylate polymerization initiated by light, reaction of a dihydrazide with a diketone to make a stablized imine, a siloxane crosslinking reaction, or a nucleophilic attack onto an electrophilic site such as reaction of a thiol or amine with an activated ester, aldol condensation, and the like. A further embodiment of this invention is the crosslinking between dendritic polymers and dendritic polymers and linear polymers or any combination thereof to form a crosslinked gel or network. The gels can be highly hydrated and hydrophilic and thus called hydrogels.

For the chemical crosslinking reaction that is non-light activating, the polymers are functionalized to contain groups that will react with each other to form the gel. For example, the dendritic polymers have been chemically modified to have more than two functional groups such nucleophilic groups, such as primary amino ($-NH_2$) groups or thiol (-SH) groups, which can react with electrophilic groups such as an acrylate, succinimidyl ester, maleimide, or aldehyde. Each functional group on a multifunctionally dendritic

polymer is capable of covalently binding with another polymer, thereby effecting crosslinking between the polymers and formation of the network.

Examples of covalently crosslinked networks can be formed by reacting an activated ester (such as a succinimidyl ester) with an amine or thiol (such as a terminal primary or secondary amine, lys, cys, etc.) Thiol or cysteine terminated dendritic structure that forms a disulfide crosslinked network with another thiol or cysteine terminated dendritic(s) or linear polymer(s) will also form a gel. Alternatively, a gel is formed during the reaction of an aldehyde functionalized small molecule or polymer and an amine or cysteine functionalized polymer. An additional method is to have a maleimide or vinylsulfone functionalized dendritic polymer react with a thiol functionalized dendritic, linear, comb, or other polymer to form the gel. A functionalized succinimidyl glutarate dendritic polymer with an acid terminated dendritic, linear, comb, or other polymer to from the gel. An acrylate functionalized polymer reacts with an amine or thiol functionalized polymer to form the crosslinked gel. A further embodiment of this invention is the use of a chemical peptide ligation reaction to create a crosslinked gel involving a dendritic polymer. In this reaction an aldehyde or aldehyde-acid reacts with a cysteine functionalized polymer to form a gel or crosslinked network.

Biodendrimers based on a core unit and branches which is composed of glycerol and lactic acid, glycerol and glycolic acid, glycerol and succinic acid, glycerol and adipic acid, and glycerol, succinic acid, and PEG represent examples of this class of polymers according to the present invention. Thus, one can build a wide range of structures as shown below. After the core is synthesized, polymers such as PEG and PLA can be attached to the core unit or to a branch to make large starburst or dendritic polymers.

The gels of the invention can be formed by applying a dendrimeric compound to a wound of a patient, and then exposing the dendrimeric compound to a polymerization agent. For example, a dendrimeric compound having acrylate groups attached to the periphery of the dendrimer is applied to a wound of a patient, and then the dendrimeric compound is exposed to ultraviolet radiation. In certain instances, a dendrimeric compound having a nucleophilic group attached to the periphery of the dendrimer is applied to a wound of a patient, and then the dendrimeric compound is exposed to a compound having electrophilic groups.

Alternatively, a polymerization agent is applied to a wound of a patient, and then the polyermization agent is exposed to a dendrimeric compound. For example, $PEG(NHS)_2$ is applied to a wound of a patient, and then $PEG(NHS)_2$ is exposed to a dendrimeric compound having a nucleophilic group attached to the periphery of the dendrimer.

Notably, the polymerization agent may a copolymer containing either nucleophilic or electrophilic endgroups. A large number of copolymers are known the art and are amendable to the present invention. In certain instances, the copolymer comprises hydrophobic and hydrophilic domains. In certain instances, the polymerization agent is a copolymer of polyethylene glycol and polypropylene glycol, wherein the copolymer has either nucleophilic or electrophilic endgroups attached to the ends of the copolymer.

Below the present invention is described by reference to specific embodiments. This description is not meant to limit the scope of the invention, but to convey the essence of the invention. Additional embodients may be readily envisioned by one of ordinary skill in the art, and such embodiments fall within the scope of the invention.

One aspect of the present invention relates to a method for preparing and administrating *in situ* a biocompatible gel ex vivo, in vitro, or in vivo, comprising:
(a) forming a reactive composition by admixing a biocompatible crosslinking polymer having two different nucleophilic groups such as sulfhydryl and amine groups where there is at least one amine or sulfhydryl group on the polymer with a biocompatible crosslinking polymer B having amine and sulfhydryl-reactive groups, and further wherein the amine and sulfhydryl-reactive groups are capable of covalent reaction with the amine and sulfhydryl groups upon admixture of polymers A and B under effective crosslinking conditions to form a gel in less than one day; and
(b) allowing the components of the reactive composition to crosslink and thereby form a gel.

Another aspect of the present invention relates to dendritic or branched polymers or copolymers composed of monomers synthesized by combining branching compounds with other linear or branched building blocks. Both components are known to be biocompatible or are natural metabolites *in vivo* including but not limited to glycerol, citric acid, lactic acid, glycolic acid, adipic acid, caproic acid, ribose, glucose, succinic acid, malic acid, amino acids, peptides, synthetic peptide analogs, poly(ethylene glycol), poly(hydroxyacids)

[e.g., PGA. PLA], including where one of the monomers is a branched structure such as glycerol combined with one of the other components.

In certain instances, the present invention relates to the aforementioned polymers derivatized with peripheral compounds possessing an olefin including but not limited to acrylate, methacrylate.

In certain instances, the present invention relates to the aforementioned polymers derivatized with peripheral compounds including but not limited to cysteine, lysine, other amino acids, or any other compounds that would provide terminal nucleophiles (including but not limited to amines, thiols, hydroxyl groups) or electrophiles (including but not limited to NHS esters, maleimides, aldehydes, ketones).

In certain instances, the present invention relates to the aforementioned polymers for subsequent polymerization/crosslinking/reaction with another linear or branched structure with either olefinic, electrophilic or nucleophilic groups, respectively to form a gel.

In certain instances, the present invention relates to the aforementioned polymers for subsequent polymerization/crosslinking/reaction with another linear or branched structure via a photopolymerization process (single or multi-photon process) to form a gel.

Another aspect of the present invention relates to a branching structure with at least three functional groups composed of but not limited to glycerol, citric acid, malic acid, amino acids, peptides, synthetic peptide analogs, or other dendritic strucutures synthesized to produce terminal olefins (including but not limited to acrylate or methacrylate groups), nucleophiles (including but not limited to amines, thiols, hydroxyl groups) or electrophiles (including but not limited to NHS esters, maleimides, aldehydes, ketones) for subsequent polymerization/crosslinking with another linear or branched structure with either olefinic, electrophilic or nucleophilic groups, respectively.

Another aspect of the present invention relates to a branching structure with at least three functional groups composed of but not limited to glycerol, citric acid, malic acid, amino acids, peptides, synthetic peptide analogs, or other dendritic structures derivatized with peripheral compounds including but not limited to cysteine, lysine, other amino acids, or any other compounds that would provide terminal olefins (including but not limited to acrylate or methacrylate groups), nucleophiles (including but not limited to amines, thiols,

hydroxyl groups) or electrophiles (including but not limited to NHS esters, maleimides, aldehydes, ketones) for subsequent polymerization/crosslinking with another linear or branched structure with either olefinic, electrophilic or nucleophilic groups, respectively.

Another aspect of the present invention relates to a branching structure composed of three lysine amino acids with four cysteine amino acids on the periphery with the structure CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl as described in the examples.

Another aspect of the present invention relates to a branching structure composed of three lysine amino acids with amines on the periphery with the structure (Lys)Lys(Lys)OMe•4HCl as described in the examples.

In certain instances, the present invention relates to the aforementioned polymers for subsequent polymerization/crosslinking/reaction with another linear or branched structure with olefinic, electrophilic or nucleophilic groups to form a gel.

In certain instances, the present invention relates to the aforementioned polymers for subsequent polymerization/crosslinking/reaction with another linear or branched structure through thiazolidine linkages to form a gel.

In certain instances, the present invention relates to the aforementioned polymers undergoing polymerization/crosslinking with a poly(ethylene glycol) molecular weight of about 200 to about 200,000 with at least two electrophilic groups.

In certain instances, the present invention relates to the aforementioned polymers undergoing polymerization/crosslinking with a poly(ethylene glycol) molecular weight of about 200 to about 200,000 with at least two nucleophilic groups

In certain instances, the present invention relates to the aforementioned polymers undergoing polymerization/crosslinking with a poly(ethylene glycol) molecular weight of about 200 to about 200,000 with functional groups including but not limited to olefins, aldehydes, maleimides, or NHS esters.

In certain instances, the present invention relates to the aforementioned polymers undergoing polymerization/crosslinking with a poly(ethylene glycol) molecular weight of about 200 to about 200,000 with aldehyde functional groups to form hydrogels through the formation of thiazolidine linkages.

In certain instances, the present invention relates to the aforementioned formulations in which each of the components are dissolved or suspended in an aqueous solution wherein

the said aqueous solution is selected from water, buffered aqueous media, saline, buffered saline, solutions of amino acids, solutions of sugars, solutions of vitamins, solutions of carbohydrates or combinations of any two or more thereof.

In certain instances, the present invention relates to the application of the aforementioned formulation through a delivery device which physically separates the components until the components are physically mixed by the end user, including but not limited to a dual barrel syringe with a mixing device.

Another aspect of the present invention relates to packaging of the aforementioned branching compounds in an aqueous solution at a preselected pH and molarity selected from the aqueous solutions described above and the packaging of the second compound in an aqueous solution at another preselected pH and molarity selected from the aqueous solutions described above. When combined, the pH and molarities of the two solutions produce a final desired solution with a different pH.

Another aspect of the present invention relates to packaging of the aforementioned branching compounds in an aqueous solution at a preselected pH and molarity selected from the aqueous solutions described above and the packaging of the second compound in an aqueous solution at another preselected pH and molarity selected from the aqueous solutions described above. The contents are packaged free of oxygen and shielded from light. When combined, the pH and molarities of the two solutions produce a final desired solution with a different pH.

Another aspect of the present invention relates to packaging of the aforementioned branching compounds as a powder and adding an aqueous solution at a preselected pH and molarity selected from the aqueous solutions described above before use. The second component may either be packaged by dissolving the second compound in an aqueous solution at another preselected pH and molarity selected from the aqueous solutions described above or packaged similar to the first compound in which the compound stored as a powder and an aqueous solution at a preselected pH and molarity selected from the aqueous solutions described above is added before use. The contents are packaged free of oxygen and shielded from light. When combined, the pH and molarities of the two solutions produce a final desired solution with a different pH.

Another aspect of the present invention relates to the storage of the aforementioned cystein terminated polymers in an acidic, oxygen free solution to minimize the formation of disulfide bonds.

Another aspect of the present invention relates to the storage of the aforementioned aldehyde terminated polymers in an acidic, oxygen free solution to maximize the percent reactivity of the polymer and minimize aldol condensation and reverse Michael additions.

Another aspect of the present invention relates to the addition of various additives that might be incorporated into the polymer formulations including, but not limited to, antioxidants, colorants, viscosity modifiers, plasticizers, small molecule carbohydrates, large molecule carbohydrates, amino acids, peptides, or other water soluble polymers (linear or branched). Such additives may be added to increase the shelf life, increase the polymerization rate, modifiy the pH or molarity of the solution, change the refractive index, modify the mechanical properties, change crosslinking density, decrease swelling, or aid in visualization.

Another aspect of the present invention relates to the addition of various additives or anti-microbial agents such has polyhexamethylene biguanide (PHMB) that might be incorporated into the polymer formulations.

Another aspect of the present invention relates to the resulting hydrogels formed by mixing the aforementioned compounds as described and prepared above.

In certain instances, the present invention relates to hydrogels formed by photopolymerization of the aforementioned compounds.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for ophthalmic applications.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as an ophthalmic sealant.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as an intraocular lens replacement.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for an injectable *in situ* polymerizing/crosslinking intraocular lens.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels to seal or repair sclerotomy incisions.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels to seal or repair corneal incisions, lacerations, perforations, ulcerations.

Another aspect of the present invention relates to the use of the polymers, branching structures, and their hydrogels to seal or close a corneal transplant with or without the use of sutures.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels to seal or repair trabeculectomy incisions or leaking blebs.

Another aspect of the present invention relates to the use of the polymers, branching structures, and their hydrogels to seal or repair blepharoplasty or skin incisions.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels to seal or repair ocular wounds or lacerations.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as a drug delivery vehicle and an adhesive/sealant to aid in the repair or sealing of an ophthalmic wound.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as a drug delivery vehicle and an adhesive/sealant to aid in the repair or sealing of an ophthalmic wound wherein the durg has antimicrobial or antibacterial properties.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels wherein the adhesive/sealant also acts as a physical barrier to prevent or reduce microbial infection.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as a drug delivery vehicle to treat one or more ophthalmic diseases.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as a drug delivery vehicle to treat glaucoma and macular degeneration.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for wound care or wound management.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels as a tissue sealant/adhesive/patch.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for reconstructive or cosmetic surgery in ophthalmolgy.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for seeding cells *in vitro* for subsequent *in vivo* placement.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for repair or restoration of cornea tissue.

Another aspect of the present invention relates to a method of using the polymers, branching structures, and their hydrogels for delivery of therapeutics.

Another aspect of the present invention relates a method of using the polymers, branching structures, and their hydrogels for drug delivery in the eye.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary branched or dendritic polymer or monomer for wound care or wound management.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymer or monomer as a tissue sealant.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for ophthalmic applications.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as an ophthalmic sealant.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as an intraocular lens replacement.

Another aspect of the present invention relates to a method of using the a crosslinkable/polymerizable/reactionary polymers, branching structures, and their hydrogels for an injectable *in situ* polymerizing/crosslinking intraocular lens replacement.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels to seal or repair sclerotomy incisions.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels to seal or repair corneal incisions, lacerations, perforations, ulcerations.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, and their hydrogels to seal or close a corneal transplant with or without the use of sutures.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels to seal or repair trabeculectomy incisions or leaking blebs.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels to seal or repair blepharoplasty or skin incisions.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels to seal or repair ocular wounds or lacerations.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as a drug delivery vehicle and an adhesive/sealant to aid in the repair or sealing of an ophthalmic wound.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as a drug delivery vehicle and an adhesive/sealant to aid in the repair or sealing of an ophthalmic wound wherein the drug has antimicrobial or antibacterial properties.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their

hydrogels wherein the adhesive/sealant also acts as a physical barrier to prevent or reduce microbial infection.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as a drug delivery vehicle to treat one or more ophthalmic diseases.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as a drug delivery vehicle to treat glaucoma and macular degeneration

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for wound care or wound management.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels as a tissue sealant/adhesive/patch.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for reconstructive or cosmetic surgery in ophthalmolgy.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for seeding cells *in vitro* for subsequent *in vivo* placement.

Another aspect of the present invention relates to a method of using crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for repair or restoration of cornea tissue.

Another aspect of the present invention relates to a method of using crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for delivery of therapeutics.

Another aspect of the present invention relates to a method of using crosslinkable/polymerizable/reactionary dendritic polymers, branching structures, and their hydrogels for drug delivery in the eye.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymer or monomer for seeding with cells and subsequent *in situ* polymerization *in vivo*.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary dendritic polymer or monomer for delivery of therapeutics while performing as a sealant/adhesive.

Another aspect of the present invention relates to a method of using a crosslinkable/polymerizable/reactionary branched or dendritic polymer for drug delivery.

Another aspect of the present invention relates to a crosslinkable/polymerizable/reactionary dendritic polymer or monomer wherein the crosslinking is of covalent, ionic, electrostatic, and/or hydrophobic nature.

Another aspect of the present invention relates to a crosslinkable dendritic polymer or monomer wherein the crosslinking reaction involves a nucleophile and electrophile.

Another aspect of the present invention relates to a crosslinkable dendritic polymer or monomer wherein the crosslinking reaction is a peptide ligation reaction.

Another aspect of the present invention relates to a crosslinkable dendritic polymer or monomer wherein the crosslinking reaction is a Diels-Alder reaction.

Another aspect of the present invention relates to a crosslinkable dendritic polymer or monomer wherein the crosslinking reaction is a Michael Addition reaction.

Another aspect of the present invention relates to a crosslinkable dendritic polymer or monomer wherein the crosslinking reaction is a photochemical reaction using a UV or vis photoinitator chromophore.

Another aspect of the present invention relates to a crosslinkable branched or dendritic polymer in combination with a linear, comb, multi-block, star, or dendritic polymer(s) as a tissue sealant/adhesive.

Another aspect of the present invention relates to a crosslinkable branched or dendritic polymer in combination with a crosslinkable linear, comb, multi-block, star, or dendritic polymer(s) for a medical or tissue engineering application.

Another aspect of the present invention relates to a crosslinkable branched or dendritic polymer in combinaton with a crosslinkable monomer(s) for a medical or tissue engineering application.

Another aspect of the present invention relates to a method of using a crosslinkable branched or dendritic polymer combined with a crosslinkable small molecule(s) (molecule weight less than about 1000 daltons) for a medical or tissue engineering application.

Another aspect of the present invention relates to a crosslinkable branched or dendritic polymer or monomer wherein the said crosslinking dendritic polymer is combined with one or more linear, comb, multi-block, star polymers or crosslinkable comb, multi-block, star polymers.

Another aspect of the present invention relates to a crosslinkable dendritic polymer or monomer wherein the final polymeric form is a gel, film, fiber, or woven sheet.

Another aspect of the present invention relates to the aforementioned polymers, branching structures, and their resulting hydrogels wherein the final polymeric form is a gel, film, fiber, or woven sheet.

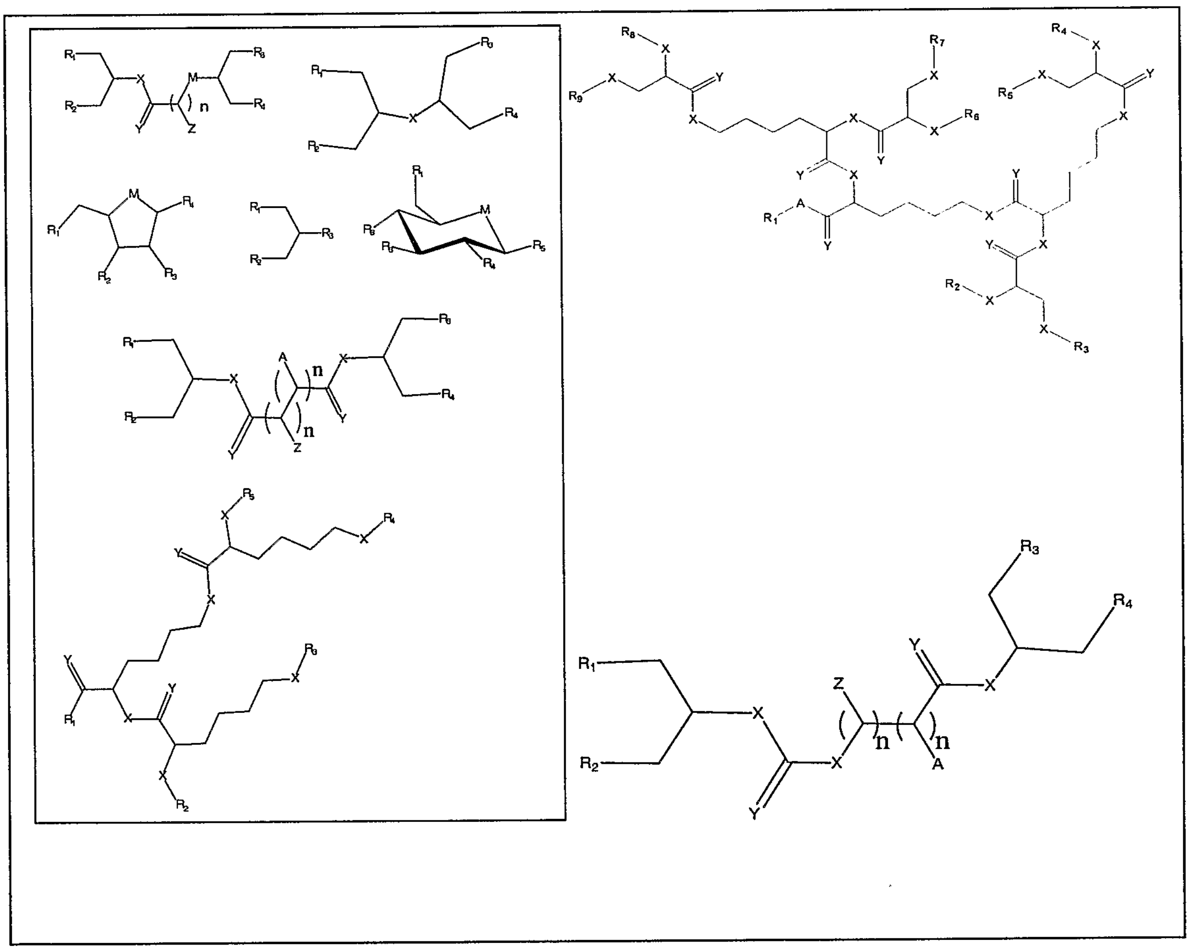
Another aspect of the present invention relates to the aforementioned polymers, branching structures, and their resulting hydrogels wherein the polymer or crosslinkable monomer is D or L configuration or a mixture.

Another aspect of the present invention relates to the aforementioned polymers, branching structures, and their resulting hydrogels wherein the branching structure, linkages and or the incorporation of aromatic or hterocyclic groups changes the refractive index.

Another aspect of the present invention relates to the aforementioned polymers, branching structures, and their hydrogels wherein the dendritic structure is asymmetric at the surface such as a surface block structure where a carboxylate acid(s) and alkyl chains, or acrylate(s) and PEG(s) are present, for example, or within the core and inner layers of the dendrimer such as amide and ester linkages in the structure.

Another aspect of the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer wherein the polymer is a star biodendritic polymer or copolymer as shown in at least one of the formulas below: where Y and X are the same or different at each occurrence and are O, S, Se, N(H), or P(H) and where R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, A or Z are the same or different and include –H, $-CH_3$, -OH, carboxylic acid,

sulfate, phosphate, aldehyde, methoxy, amine, amide, thiol, disulfide, straight or branched chain alkane, straight or branched chain alkene, straight or branched chain ester, straight or branched chain ether, straight or branched chain silane, straight or branched chain urethane, straight or branched chain, carbonate, straight or branched chain sulfate, straight or branched chain phosphate, straight or branched chain thiol urethane, straight or branched chain amine, straight or branched chain thiol urea, straight or branched chain thiol ether, straight or branched chain thiol ester, or any combination thereof.



Another aspect of the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer where the straight or branched chain is of about 1-50 carbon atoms wherein the chain is fully saturated, fully unsaturated or any combination therein

In certain instances, the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer where the straight or branched chain is of about

1-50 carbon atoms wherein the chain is fully saturated, fully unsaturated or any combination therein.

In certain instances, the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer wherein straight or branched chains are the same number of carbons or different wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, A or Z are any combination of the linkers including ester, silane, urea, amide, amine, carbamate, urethane, thiol-urethane, carbonate, thio-ether, thio-ester, sulfate, phosphate and ether.

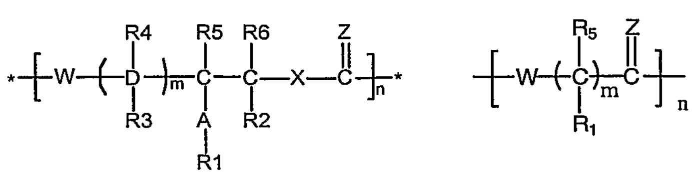
In certain instances, the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer which includes at least one chain selected from the group consisting of hydrocarbons, flourocarbons, halocarbons, alkenes, and alkynes.

In certain instances, the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer which includes at least one chain selected from the group consisting of linear and dendritic polymers.

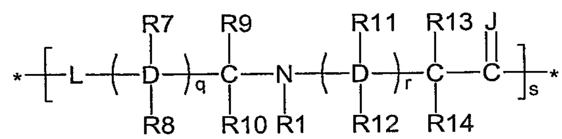
In certain instances, the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer wherein said linear and dendritic polymers include at least one selected from the group consisting of polyethers, polyesters, polyamines, polyacrylic acids, polycarbonates, polyamino acids, polynucleic acids and polysaccharides of molecular weight ranging from about 200-1,000,000, and wherein said chain contains 0, 1 or more than 1 photopolymerizable group.

Another aspect of the present invention relates to a crosslinkable or noncrosslinkable polymer, wherein the polyether is PEG, and wherein the polyester is PLA, PGA or PLGA.

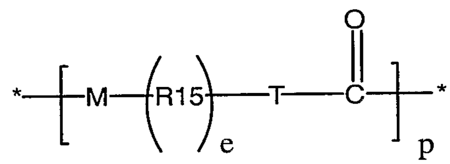
Another aspect of the present invention relates to a linear polymer wherein the chain is a polymer or copolymer of a polyester, polyamide, polyether, or polycarbonate of or the aforementioned polymer in combination with a polyester, polyamide, polyether, or polycarbonate of:



Structure I



Structure II



Structure III

In certain instances, the present invention relates to the aforementioned polymer comprised of repeating units of general Structure I, where A is O, S, Se, or N-R_7.

In certain instances, the present invention relates to the aforementioned polymer, where W, X, and Z are the same or different at each occurrence and are O, S, Se, N(H), or P(H).

In certain instances, the present invention relates to the aforementioned polymer, where R_1 is hydrogen, a straight or branched alkyl chain of about 1-20 carbons, cycloalkyl, aryl, olefin, silyl, alkylsilyl, arylsilyl, alkylaryl, or arylalkyl group.

In certain instances, the present invention relates to the aforementioned polymer, where R_1 is hydrogen, a straight or branched alkyl chain of about 1-20 carbons, cycloalkyl, aryl, olefin, silyl, alkylsilyl, arylsilyl, alkylaryl, or arylalkyl group substituted internally or terminally by one or more hydroxyl, hydroxyether, carboxyl, carboxyester, carboxyamide, amino, mono- or di-substituted amino, thiol, thioester, sulfate, phosphate, phosphonate, or halogen substituents.

In certain instances, the present invention relates to the aforementioned polymer, where R_1 is a polymer (such as poly(ethylene glycol), poly(ethylene oxide), or a poly(hydroxyacid)), a carbohydrate, a protein, a polypeptide, an amino acid, a nucleic acid, a nucleotide, a polynucleotide, any DNA or RNA segment, a lipid, a polysaccharide, an antibody, a pharmaceutical agent, or any epitope for a biological receptor.

In certain instances, the present invention relates to the aforementioned polymer, where R_1 is a photocrosslinkable, chemically, or ionically crosslinkable group.

In certain instances, the present invention relates to the aforementioned polymer, in which D is a straight or branched alkyl chain of about 1-5 carbons, m is 0 or 1, and R_2, R_3, R_4, R_5, R_6, and R_7 are the same or different at each occurrence and are hydrogen, a straight or branched alkyl chain of about 1-20 carbons, cycloalkyl, aryl, alkoxy, aryloxy, olefin, alkylamine, dialkylamine, arylamine, diarylamine, alkylamide, dialkylamide, arylamide, diarylamide, alkylaryl, or arylalkyl group.

In certain instances, the present invention relates to the aforementioned polymer comprised of repeating units of General Structure II, where L, N, and J are the same or different at each occurrence and are O, S, Se, N(H), or P(H).

In certain instances, the present invention relates to the aforementioned polymer where R_1 is hydrogen, a straight or branched alkyl chain of about 1-20 carbons, cycloalkyl, aryl, olefin, silyl, alkylsilyl, arylsilyl, alkylaryl, or arylalkyl group.

In certain instances, the present invention relates to the aforementioned polymer where R_1 is hydrogen, a straight or branched alkyl chain of about 1-20 carbons, cycloalkyl, aryl, olefin, silyl, alkylsilyl, arylsilyl, alkylaryl, or arylalkyl group substituted internally or terminally by one or more hydroxyl, hydroxyether, carboxyl, carboxyester, carboxyamide, amino, mono- or di-substituted amino, thiol, thioester, sulfate, phosphate, phosphonate, or halogen substituents.

In certain instances, the present invention relates to the aforementioned polymer where R_1 is a polymer selected from the group consisting of poly(ethylene glycols), poly(ethylene oxides), and poly(hydroxyacids, or is a carbohydrate, a protein, a polypeptide, an amino acid, a nucleic acid, a nucleotide, a polynucleotide, a DNA or RNA segment, a lipid, a polysaccharide, an antibody, a pharmaceutical agent, or an epitope for a biological receptor.

In certain instances, the present invention relates to the aforementioned polymer where R_1 is a photocrosslinkable, chemically, or ionically crosslinkable group.

In certain instances, the present invention relates to the aforementioned polymer, where D is a straight or branched alkyl chain of about 1-5 carbons, q and r are the same or different at each occurrence and are 0 or 1, and R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, and R_{14} are the same or different at each occurrence and are hydrogen, a straight or branched alkyl chain of about 1-20 carbons, cycloalkyl, aryl, alkoxy, aryloxy, olefin, alkylamine, dialkylamine,

arylamine, diarylamine, alkylamide, dialkylamide, arylamide, diarylamide, alkylaryl, or arylalkyl group.

In certain instances, the present invention relates to the aforementioned block or random copolymer comprised of repeating units of general Structure III, where M, T, and Q are the same or different at each occurrence and are O, S, Se, N(H), or P(H), e is 0 or 1-9, and R_{15} is a straight or branched alkyl chain of about 1-5 carbons, unsubstituted or substituted with one or more hydroxyl, hydroxyether, carboxyl, carboxyester, carboxyamide, amino, mono- or di-substituted amino, thiol, thioester, sulfate, phosphate, phosphonate, or halogen substituents

In certain instances, the present invention relates to the aforementioned block or random copolymer comprised of repeating units of general Structure III, where M, T, and Q are the same or different at each occurrence and are O, S, Se, N(H), or P(H), and R_{15} is a straight or branched alkyl chain of about 1-5 carbons, unsubstituted or substituted with one or more hydroxyl, hydroxyether, carboxyl, carboxyester, carboxyamide, amino, mono- or di-substituted amino, thiol, thioester, sulfate, phosphate, phosphonate, or halogen substituents.

In certain instances, the present invention relates to the aforementioned block or random copolymer comprised of repeating units of general Structure III, where M, T, and Q are the same or different at each occurrence and are O, S, Se, N(H), or P(H), and R15 is a straight or branched alkyl chain of about 1-5 carbons, unsubstituted or substituted with one or more hydroxyl, hydroxyether, carboxyl, carboxyester, carboxyamide, amino, mono- or di-substituted amino, thiol, thioester, sulfate, phosphate, phosphonate, or halogen substituents.

Another aspect of the present invention relates to a higher order block or random copolymer comprised of three or more different repeating units, and having one or more repeating units described above, such as a polyglyerol glycine carbonate-polyglycerol succinic acid copolymer.

Another aspect of the present invention relates to a block or random copolymer as described above, which includes at least one terminal crosslinkable group selected from the group consisting of amines, thiols, amides, phosphates, sulphates, hydroxides, alkenes, and alkynes.

In certain instances, the present invention relates to the aforementioned block or random copolymer where X, Y, M is O, S, N-H, N-R, and wherein R is –H, CH_2, CR_2, Se or an isoelectronic species of oxygen.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein an amino acid(s) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein a polypeptide(s) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein an antibody(ies) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein a nucleotide(s) is attached to R_1, R_2, R_3, R_4, R_5 A, and/or Z.

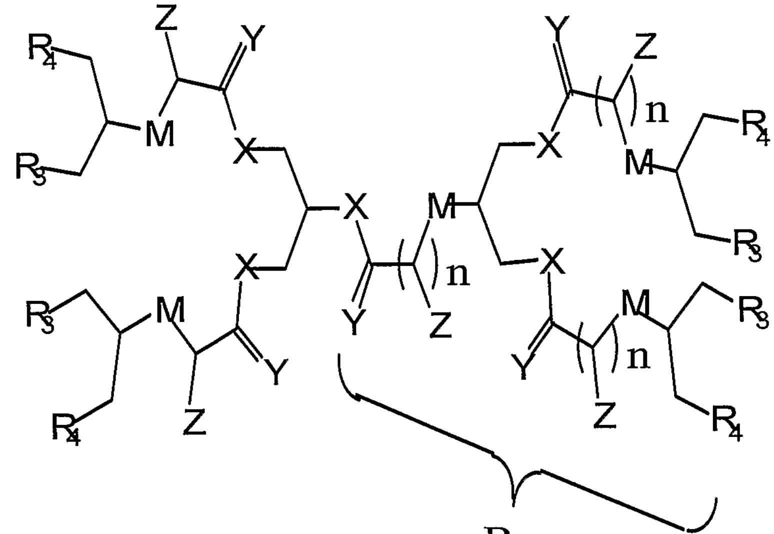
In certain instances, the present invention relates to the aforementioned block or random copolymer wherein a nucleoside(s) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein an oligonucleotide(s) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein a ligand(s) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z that binds to a biological receptor.

In certain instances, the present invention relates to the aforementioned block or random copolymer wherein a pharmaceutical agent(s) is attached to R_1, R_2, R_3, R_4, R_5, A, and/or Z.

In certain instances, the present invention relates to the aforementioned crosslinkable or noncrosslinkable polymer or copolymer wherein the polymer is a dendritic macromolecule including at least one polymer selected from the group consisting of dendrimers, hybrid linear-dendrimers, dendrons, or hyperbranched polymers according to one of the general formulas or such similar structures below: where R_3, R_4, which may be the same or different, are a repeat pattern of B, and n is about 0 to 50.



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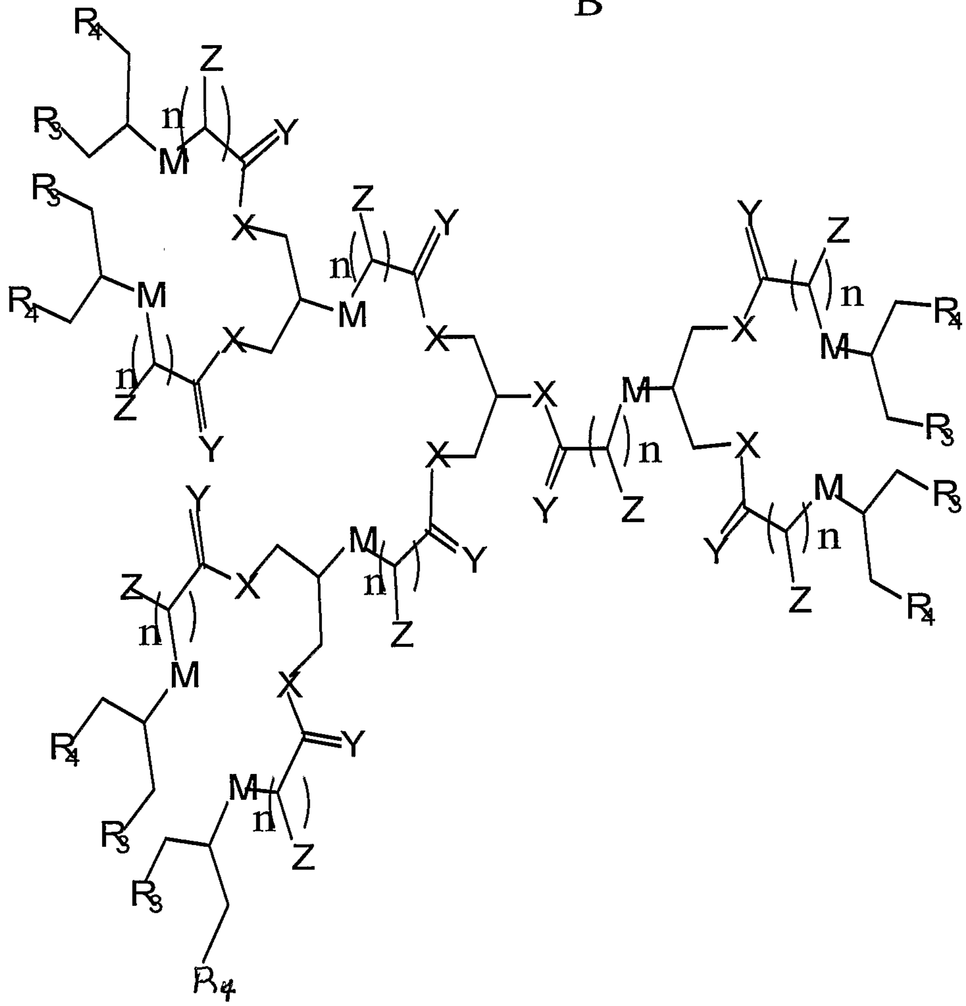
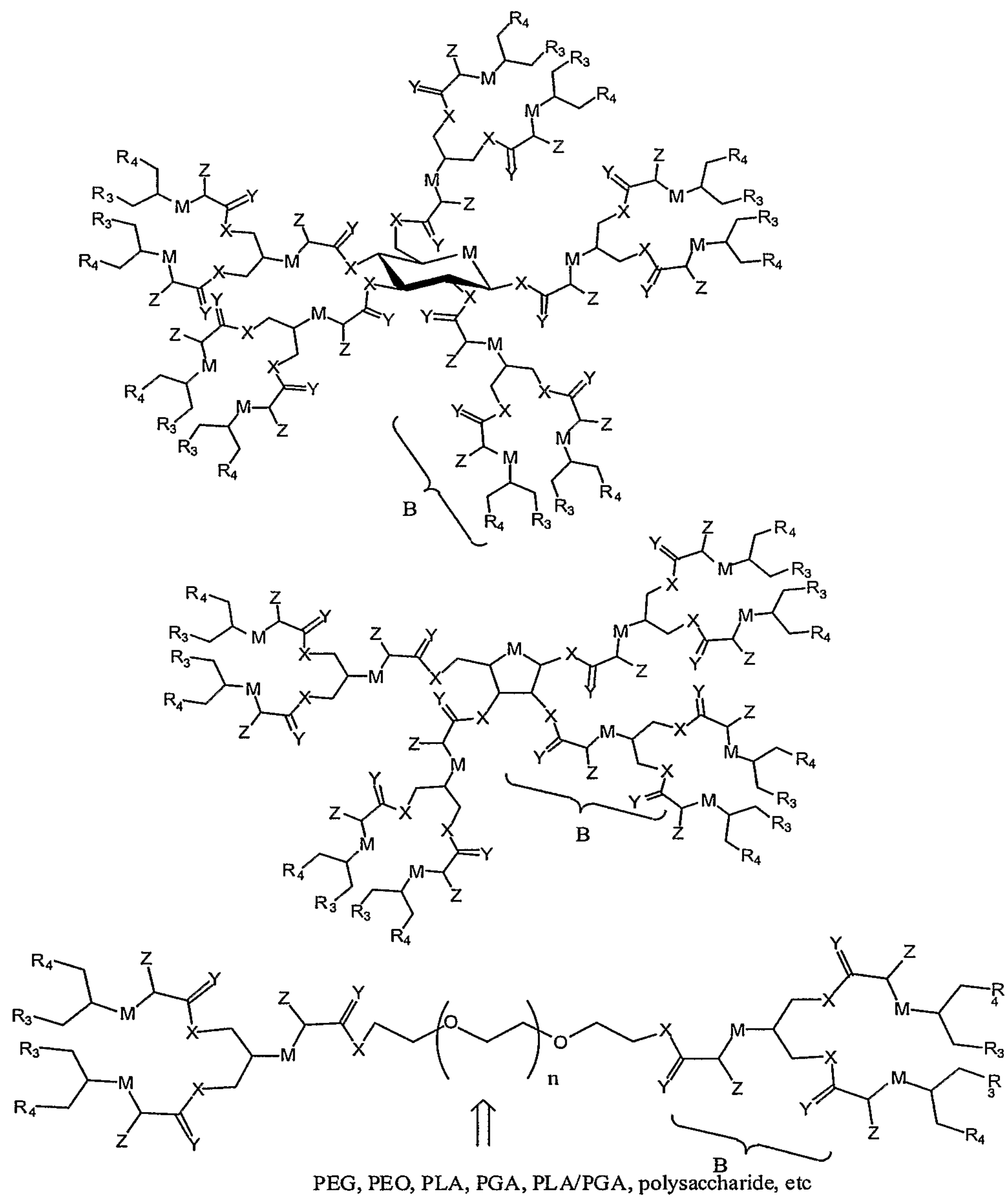
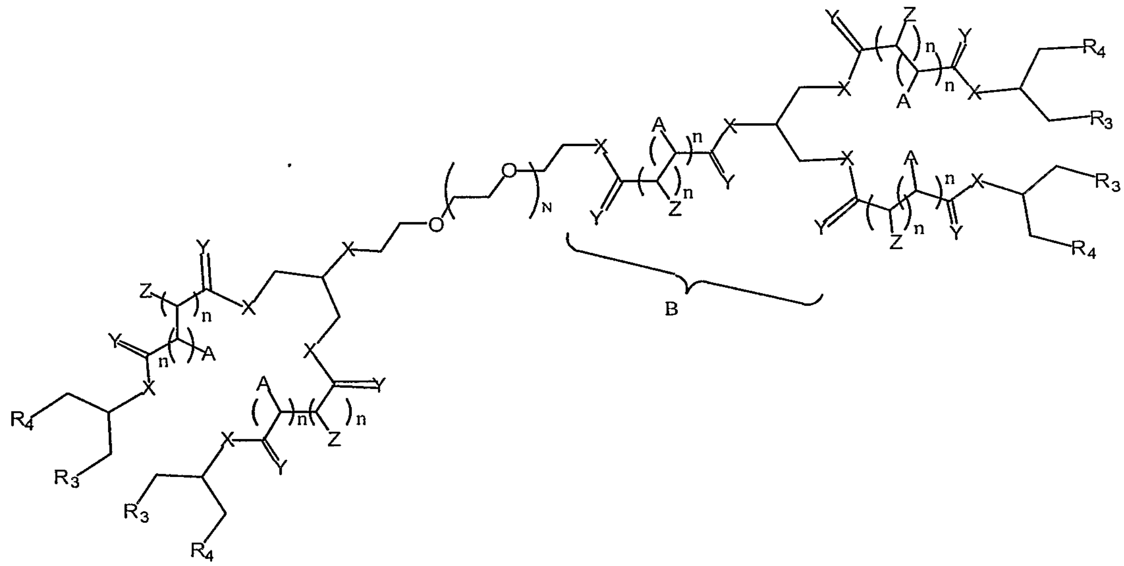
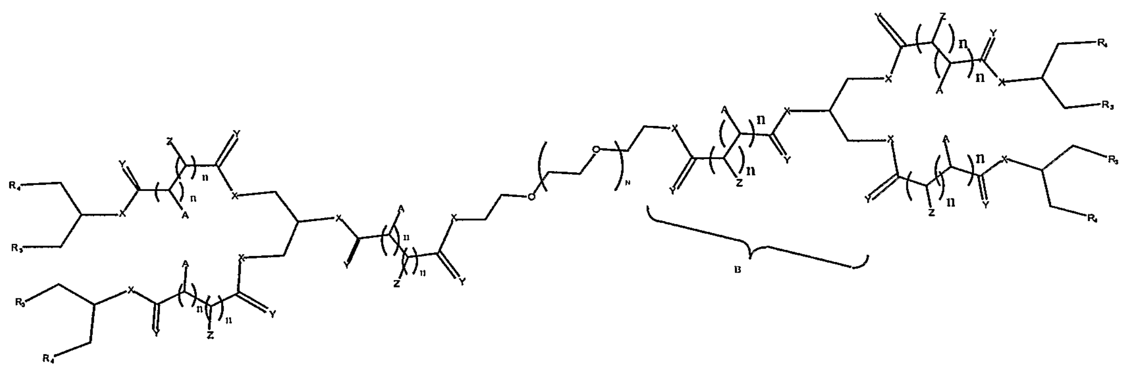
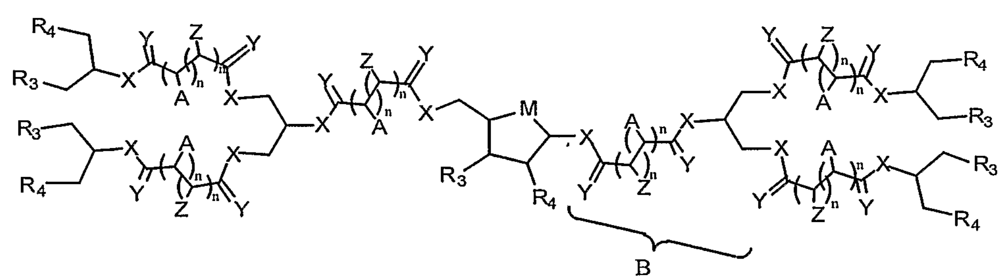
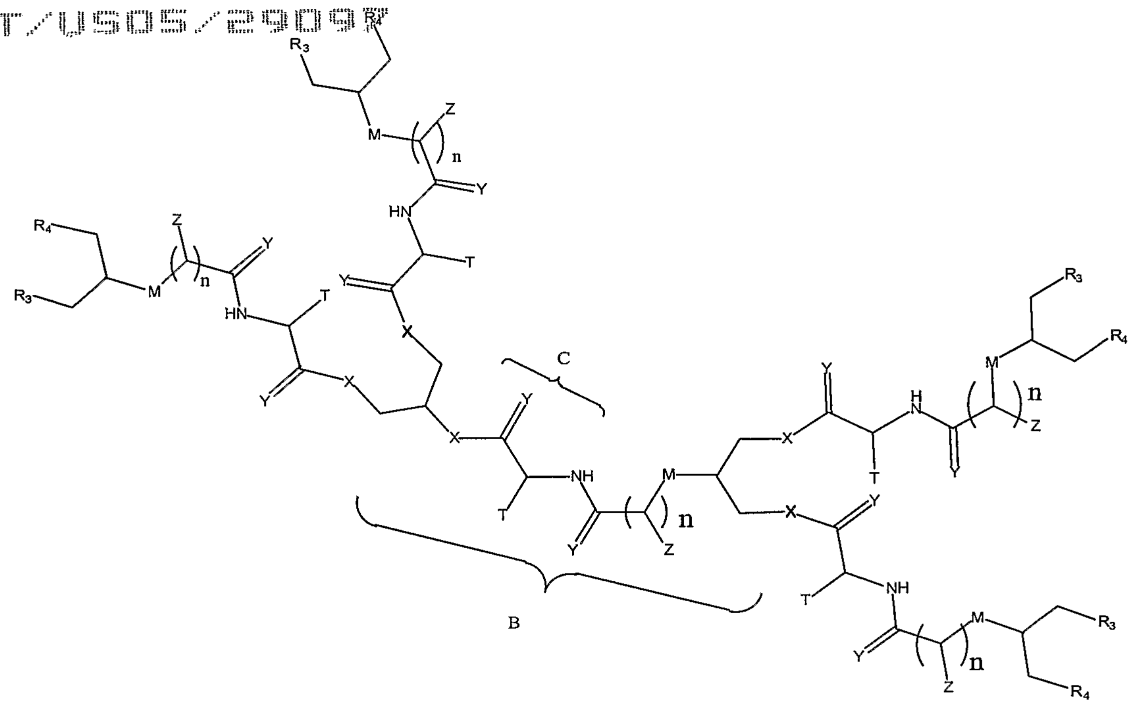


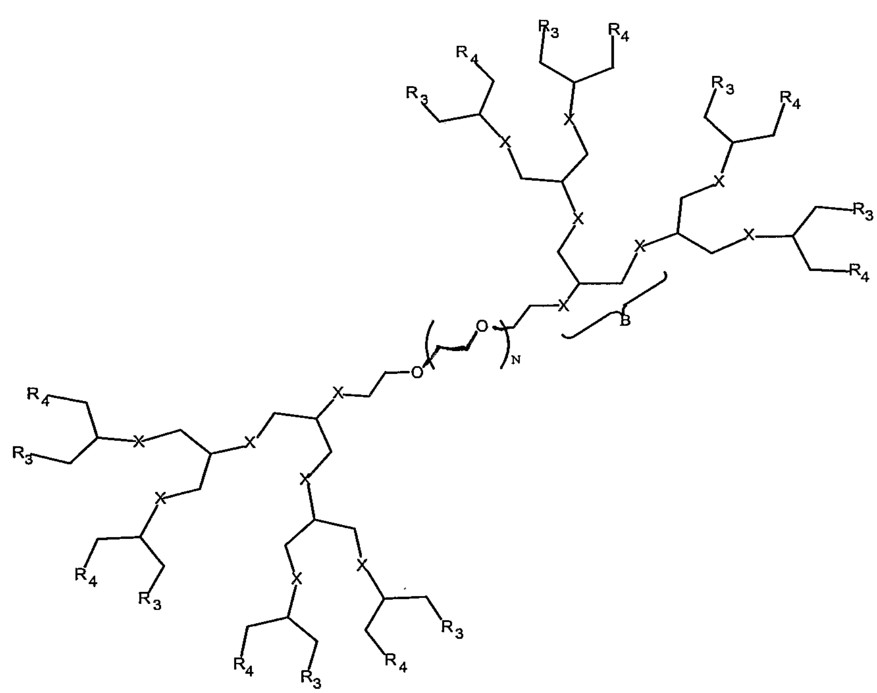

B
B
B
PEG, PEO, PLA, PGA, PLA/PGA, polysaccharide, etc

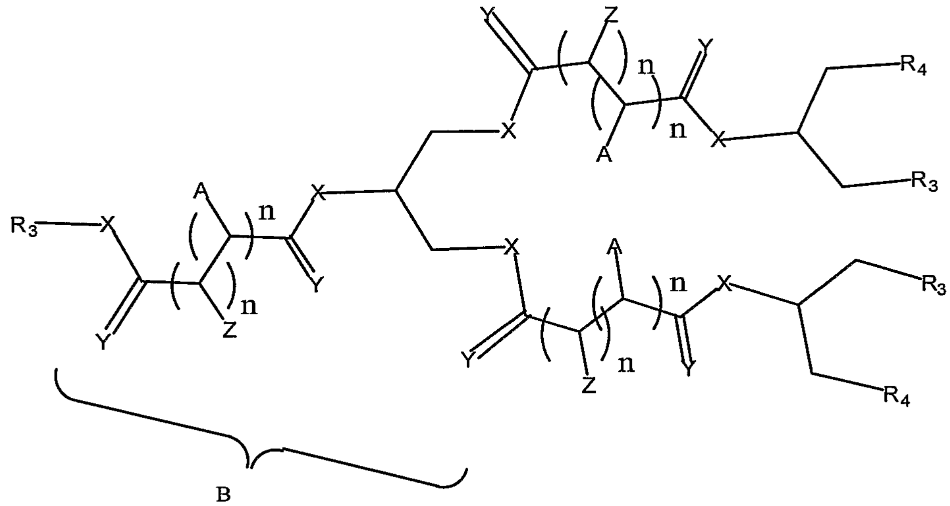











R3
R4
X
Y
Z
A
n
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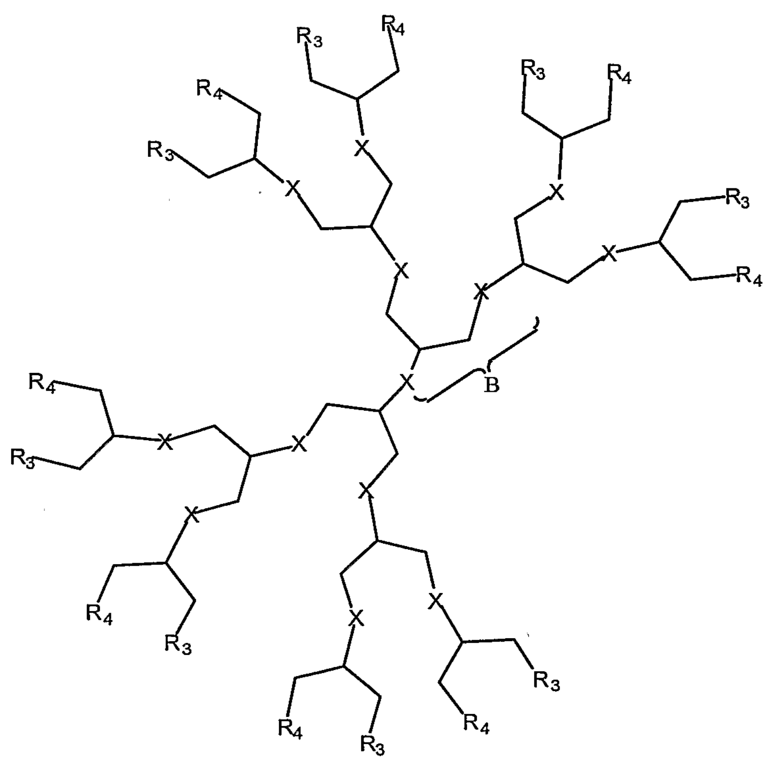
R3
R4
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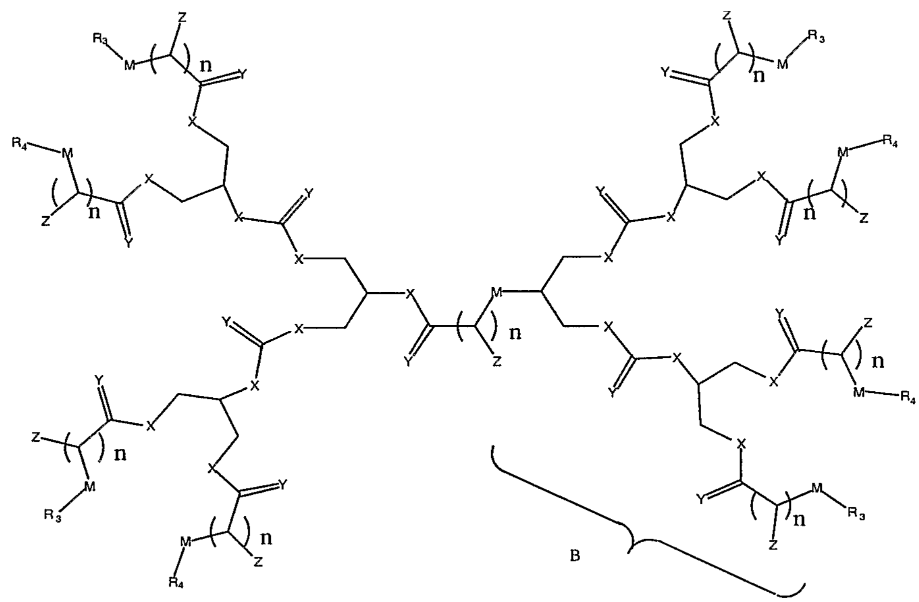

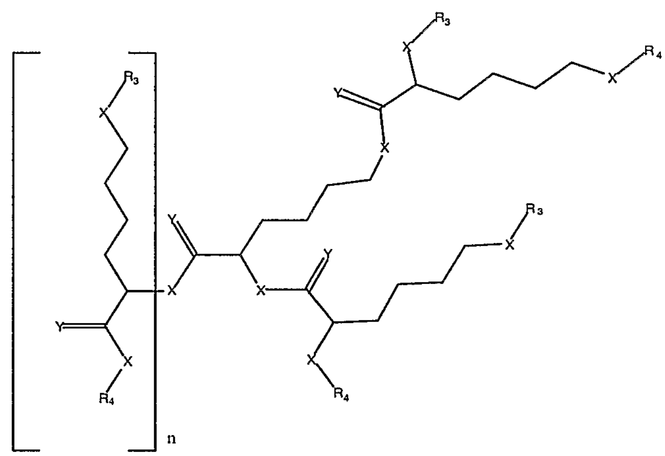

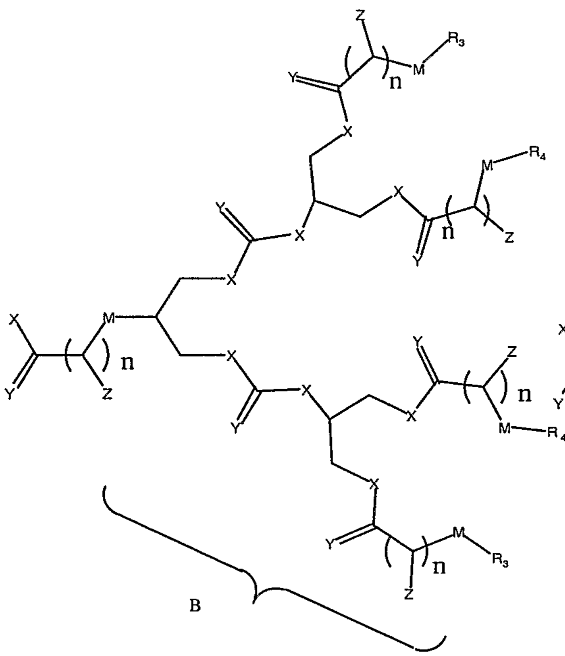
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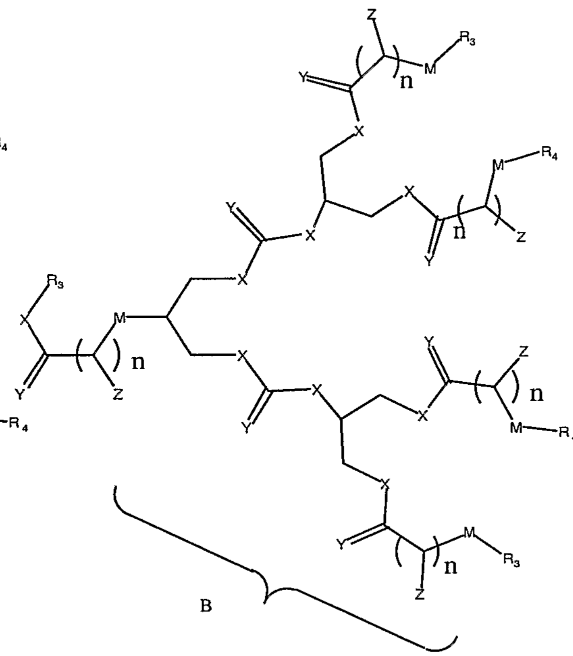
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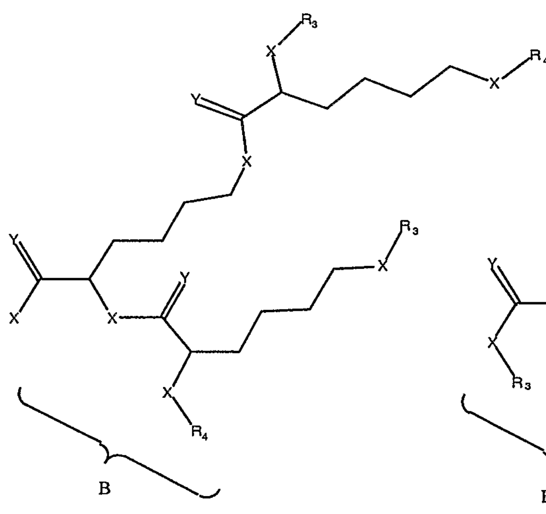
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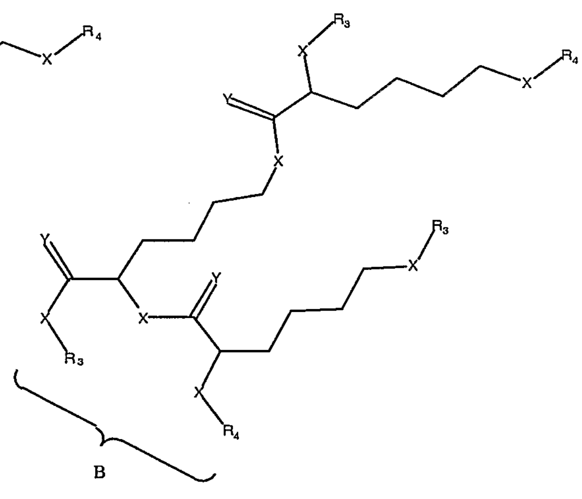
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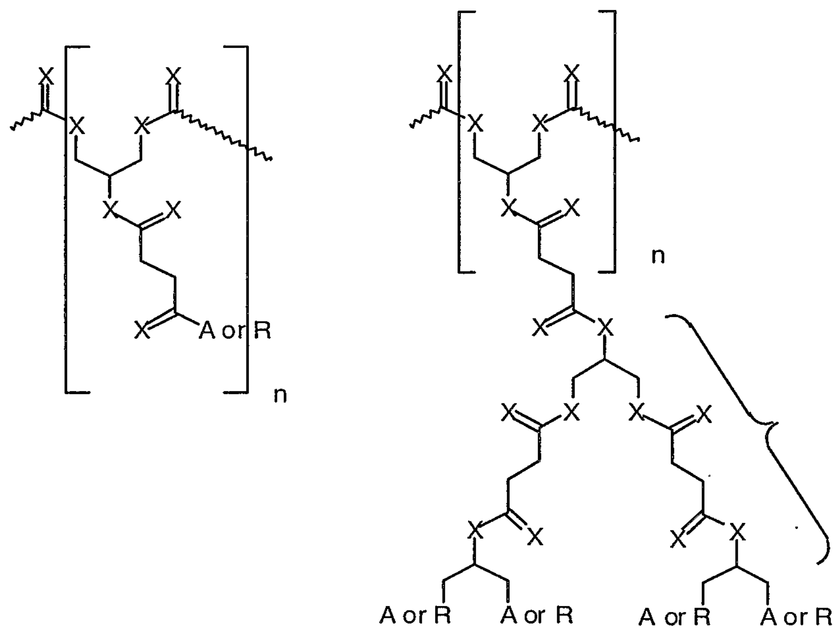


In certain instances, the present invention relates to the aforementioned polymer, wherein X, Y, M is O, S, N-H, N-R, wherein R is –H, CH_2, CR_2 or a chain as defined above, Se or any isoelectronic species of oxygen

In certain instances, the present invention relates to the aforementioned polymer, wherein X, Y, M is O, S, N-H, N-R, wherein R is –H, CH_2, CR_2 or a chain as defined above, Se or any isoelectronic species of oxygen.

In certain instances, the present invention relates to the aforementioned polymer where R_3 and R_4 are carboxylic acid with a protecting group such as but not limited to a phthalimidomethyl ester, a t-butyldimethylsilyl ester, or a t-butyldiphenylsilyl ester.

In certain instances, the present invention relates to the aforementioned polymer where R_3, R_4, A, and Z are the same or different, R_3 and R_4 are repeated a certain number of times, and terminate in –H, -OH, -CH_3, carboxylic acid, sulfate, phosphate, aldehyde, activated ester, methoxy, amine, amide, thiol, disulfide, straight or branched chain alkane, straight or branched chain alkene, straight or branched chain ester, straight or branched chain ether, straight or branched chain silane, straight or branched chain urethane, straight or branched chain, carbonate, straight or branched chain sulfate, straight or branched chain phosphate, straight or branched chain thiol urethane, straight or branched chain amine, straight or branched chain thiol urea, straight or branched chain thiol ether, straight or

branched chain thiol ester, or any combination thereof, and wherein c is a natural or un-natural amino acid.

In certain instances, the present invention relates to the aforementioned polymer having a straight or branched chain of 1-50 carbon atoms and wherein the chain is fully saturated, fully unsaturated or any combination therein.

In certain instances, the present invention relates to the aforementioned polymer wherein straight or branched chains are the same number of carbons or different and wherein R_3, R_4, A, Z are any combination of linkers selected from the group consisting of esters, silanes, ureas, amides, amines, urethanes, thiol-urethanes, carbonates, carbamates, thio-ethers, thio-esters, sulfates, phosphates and ethers.

In certain instances, the present invention relates to the aforementioned polymer wherein chains include at least one selected from hydrocarbons, flourocarbons, halocarbons, alkenes, and alkynes.

In certain instances, the present invention relates to the aforementioned polymer wherein said chains include polyethers, polyesters, polyamines, polyacrylic acids, polyamino acids, polynucleic acids and polysaccharides of molecular weight ranging from 200-1,000,000, and wherein said chain contains 1 or more crosslinkable or photopolymerizable group.

In certain instances, the present invention relates to the aforementioned polymer wherein the chains include at least one of PEG, PLA, PGA, PGLA, and PMMA.

In certain instances, the present invention relates to the aforementioned block or random copolymer, which includes at least one terminal crosslinkable or photopolymerizable group selected from the group consisting of amines, thiols, amides, phosphates, sulphates, hydroxides, alkenes, activated esters, malemides, aldehydes, and alkynes.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with amino acid(s), such as cysteine, attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with polypeptide(s) attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with an antibody(ies) or single chain antibody(ies) attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with a nucleotide(s) attached to Z, A, R_3, and/or R_4..

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with a nucleoside(s) attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with oligonucleotide(s) attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with ligand(s) attached to Z, A, R_3, and/or R_4 that binds to a biological receptor.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with a pharmaceutical agent(s) attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with a pharmaceutical agent attached to Z, A, R_3, and/or R_4 and is at least one selected from the group consisting of antibacterial, anticancer, anti-inflammatory, and antiviral.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times to produce a polymer in which a pharmaceutical agent(s) is encapsulated or chemically bound to the polymer.

In certain instances, the present invention relates to the aforementioned polymer wherein camptothecin or a deriviative of campothethcin is encapsulated

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with a carbohydrate(s) attached to Z, A, R_3, and/or R_4.

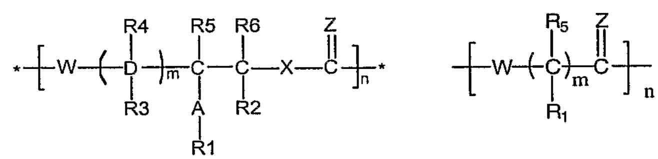
In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with a PET or MRI contrast agent(s) attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein the contrast agent is Gd(DPTA).

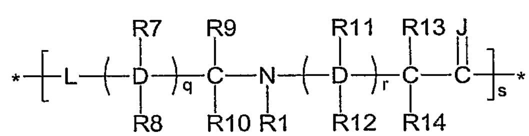
In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with an iodated compound for X-ray imagaging attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein R_3 and R_4 are repeated a certain number of times and terminates with the carbohydrate mannose or sialic acid attached to the polymer.

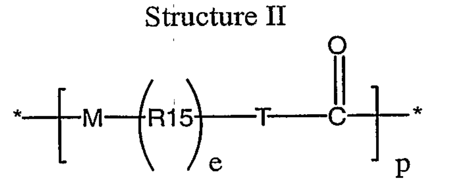
In certain instances, the present invention relates to the aforementioned polymer which includes a polymer or copolymer of a polyester, polyamide, polyether, or polycarbonate at the center or periphery of the polymers above taken from the structures below.



Structure I



Structure II



Structure III

In certain instances, the present invention relates to the aforementioned polymer block or random copolymer which includes at least one terminal or internal crosslinkable

group selected from the group consisting of amines, thiols, amides, phosphates, sulphates, hydroxides, alkenes, and alkynes.

In certain instances, the present invention relates to the aforementioned polymer wherein X, Y, M is O, S, N-H, N-R, wherein R is –H, CH_2, CR_2 or a chain as defined above, Se or any isoelectronic species of oxygen.

In certain instances, the present invention relates to the aforementioned polymer wherein an amino acid(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a polypeptide(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein an antibody(ies) or single chain antibody(ies) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a nucleotide(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a nucleoside(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein an oligonucleotide(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a ligand(s) is attached to Z, A, R_3, and/or R_4 that binds to a biological receptor.

In certain instances, the present invention relates to the aforementioned polymer wherein a pharmaceutical agent(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a carbohydrate(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a PET or MRI contrast agent(s) is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein the contrast agent is Gd(DPTA).

In certain instances, the present invention relates to the aforementioned polymer wherein an iodated compound(s) for X-ray imagaging is attached to Z, A, R_3, and/or R_4.

In certain instances, the present invention relates to the aforementioned polymer wherein a pharmaceutical agent(s) is attached to Z, A, R_3, and/or R_4 and is at least one selected from the group consisting of antibacterial, anticancer, anti-inflammatory, and antiviral.

In certain instances, the present invention relates to the aforementioned polymer wherein the carbohydrate is mannose or sialic acid is covalently attached to the polymer.

Another aspect of the present invention relates to a surgical procedure which comprises using a photopolymerizable, or chemically crosslinkable, or non-covalently crosslinkable dendritic polymer or copolymer.

Another aspect of the present invention relates to an ophthalimic surgical procedure wherein said dendritic polymer or copolymer is dissolved or suspended in an non-aqueous liquid such as soybean oil, mineral oil, corn oil, rapeseed oil, coconut oil, olive oil, saflower oil, cottonseed oil, aliphatic, cycloaliphatic or aromatic hydrocarbons having 4-30 carbon atoms, aliphatic or aromatic alcohols having 1-30 carbon atoms, aliphatic or aromatic esters having 2-30 carbon atoms, alkyl, aryl or cyclic ethers having 2-30 carbon atoms, alkyl or aryl halides having 1-30 carbon atoms and optionally having more than one halogen substituent, ketones having 3-30 carbon atoms, polyalkylene glycol or combinations of any two or more thereof.

In certain instances, the present invention relates to the ophthalimic surgical procedure wherein the supramolecular structure of the dendrimer is an emulsion.

In certain instances, the present invention relates to the dendritic polymer or copolymer which optionally contains at least one stereochemical center.

In certain instances, the present invention relates to the dendritic polymer or copolymer which is of D or L configuration.

In certain instances, the present invention relates to the dendritic polymer or copolymer wherein the final dendritic polymer or monomer is chiral or is achiral.

In certain instances, the present invention relates to the dendritic polymer or copolymer which contains at least one site where the branching is incomplete.

In certain instances, the present invention relates to a crosslinkable/photocrosslinkable/reactionary dendritic polymer or copolymer which contains at least one site where the branching is incomplete.

In certain instances, the present invention relates to a crosslinkable/photocrosslinkable/reactionary dendritic polymer or copolymer which contains at least one site where the branching is incomplete which forms a hydrogel.

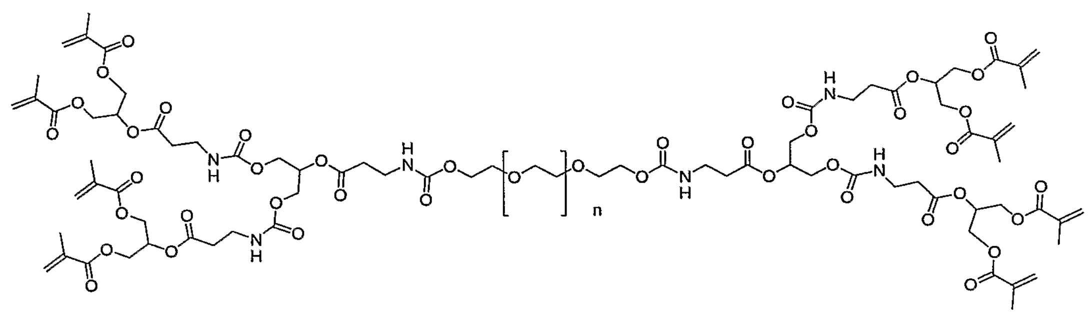
In certain instances, the present invention relates to a crosslinkable/photocrosslinkable/reactionary dendritic polymer or copolymer which contains at least one site where the branching is incomplete and used in an ophthalmic surgical procedure(s).

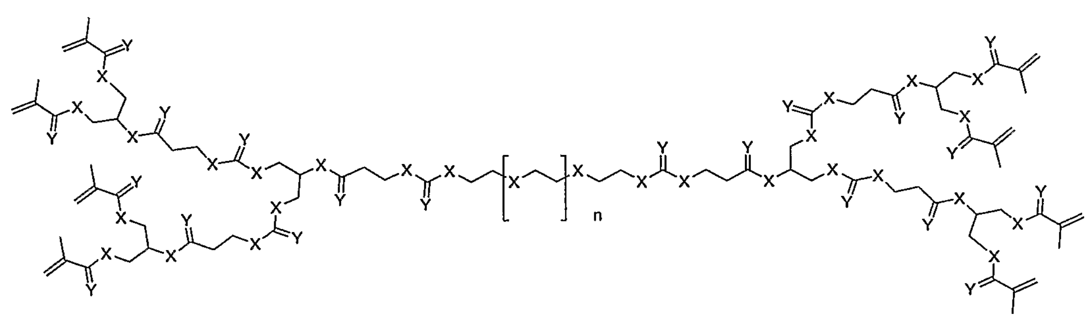
In certain instances, the present invention relates to a crosslinkable/photocrosslinkable/reactionary dendritic polymer or copolymer which contains at least one site where the branching is incomplete and used for drug delivery.

In certain instances, the present invention relates to a crosslinkable/photocrosslinkable/reactionary dendritic polymer or copolymer which contains at least one site where the branching is incomplete and used as a lens.

In certain instances, the present invention relates to a dendritic polymer or copolymer made by a convergent or divergent synthesis.

In certain instances, the dendritic polymer of the invention relates to





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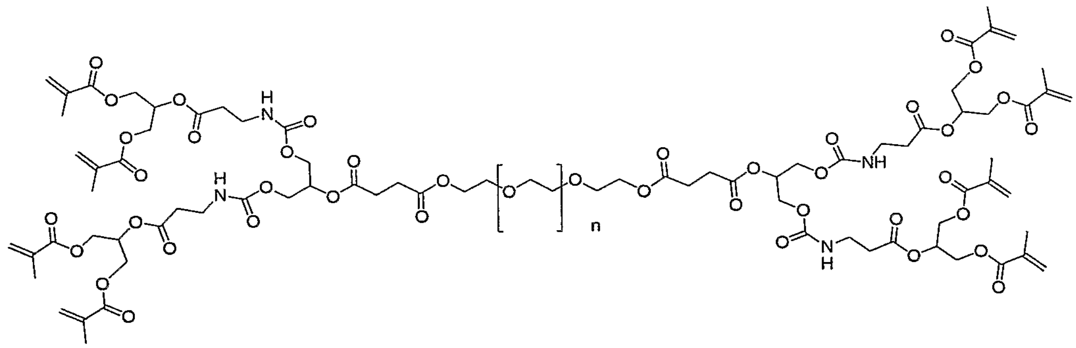

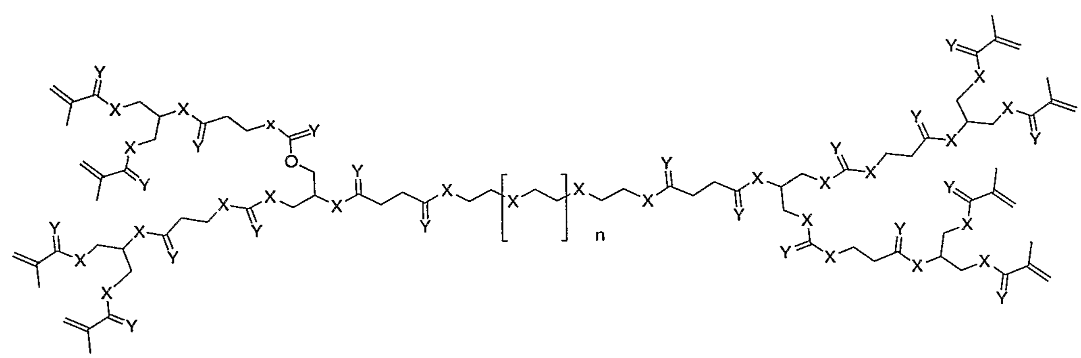

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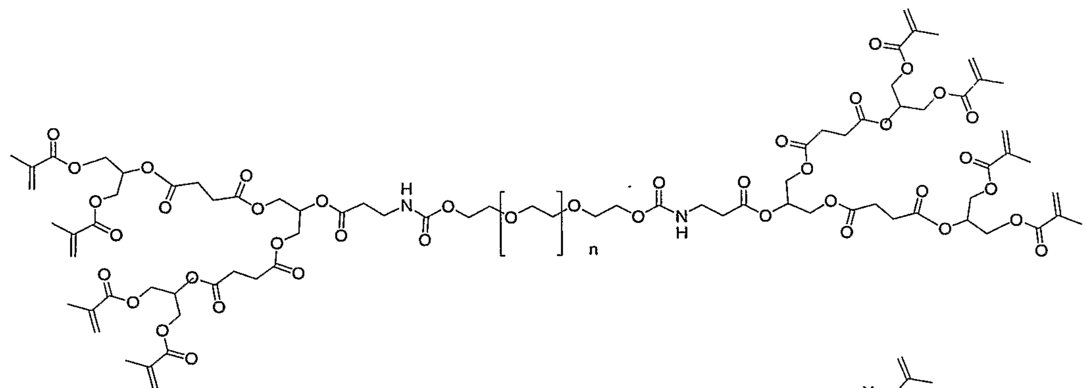

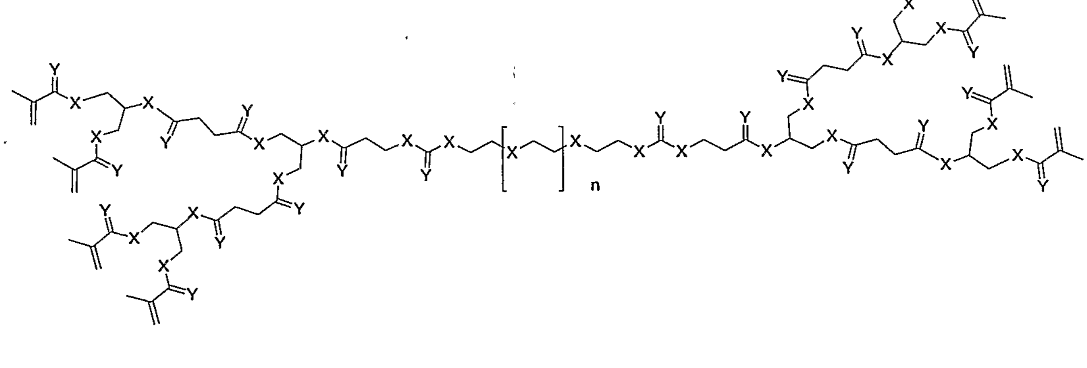

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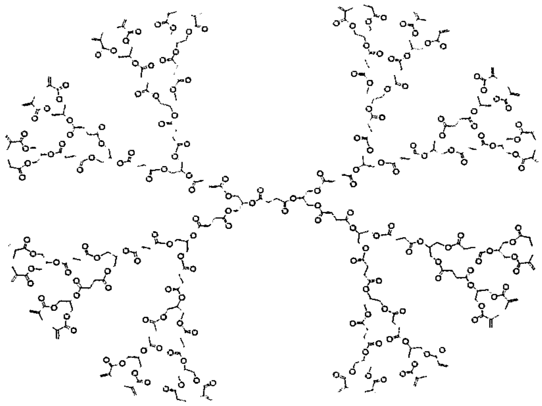
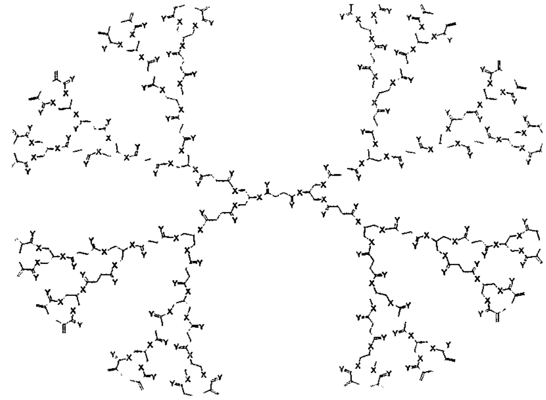
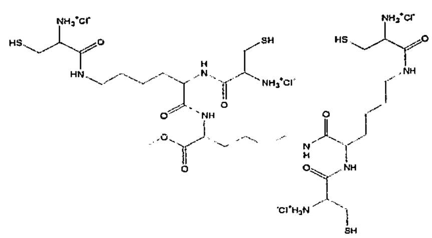
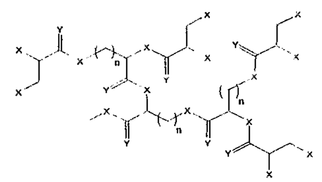
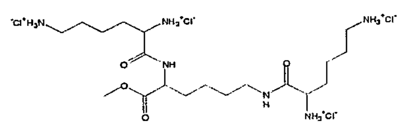
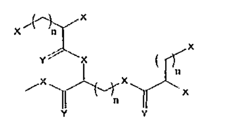


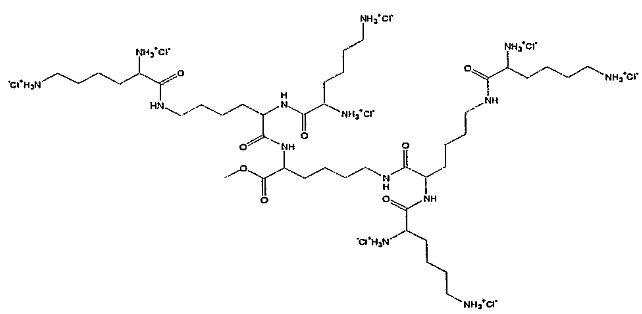


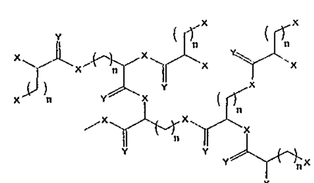


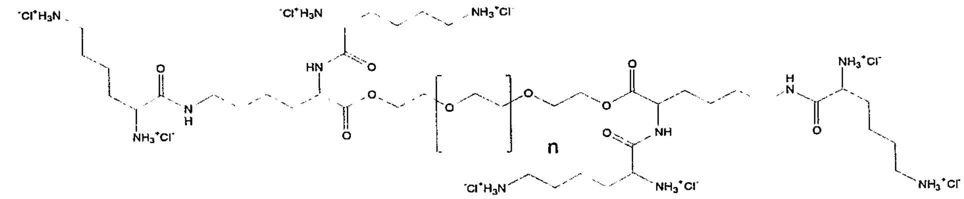


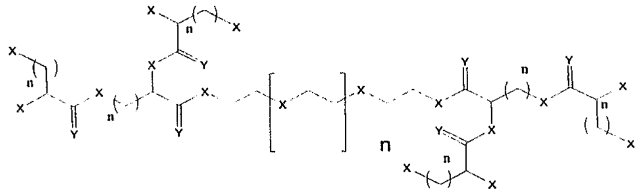


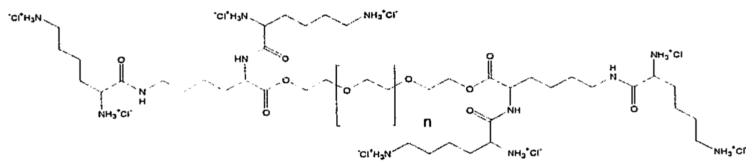


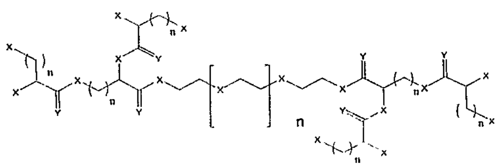


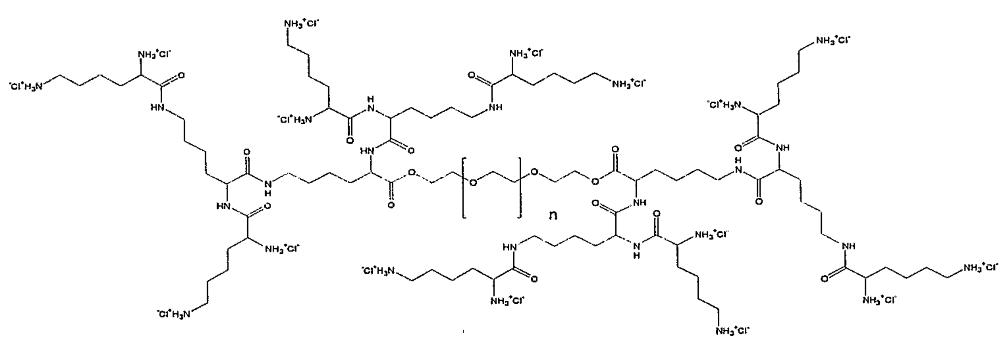


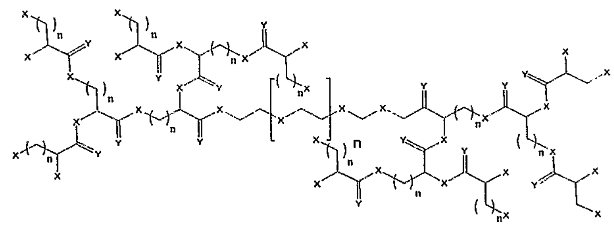


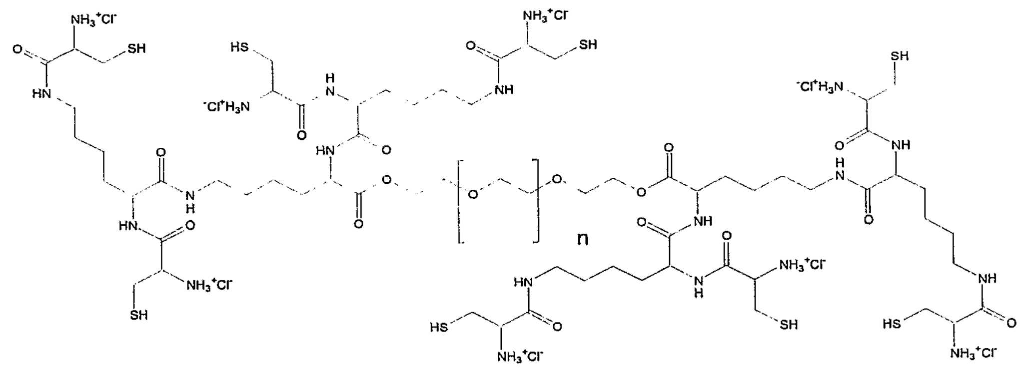


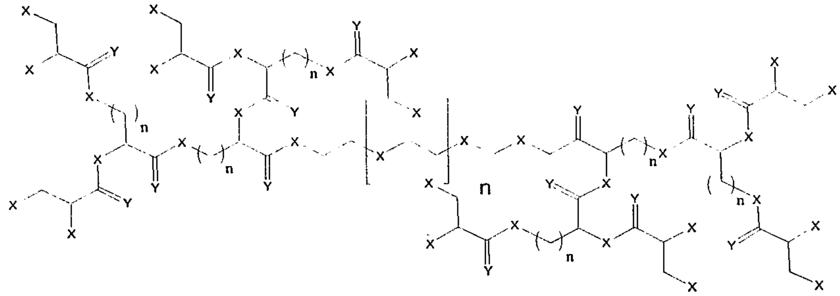


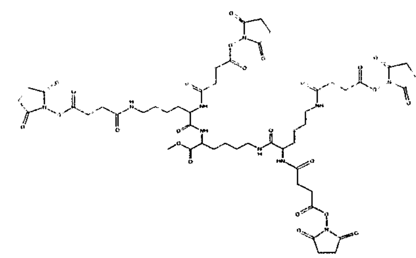


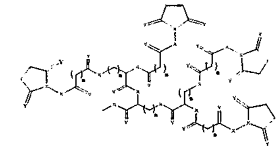


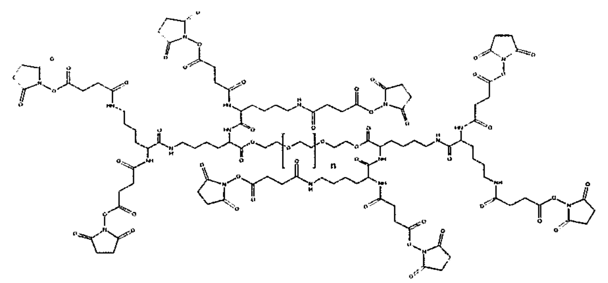


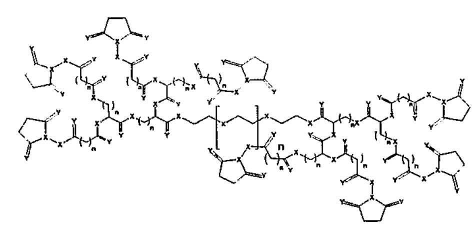


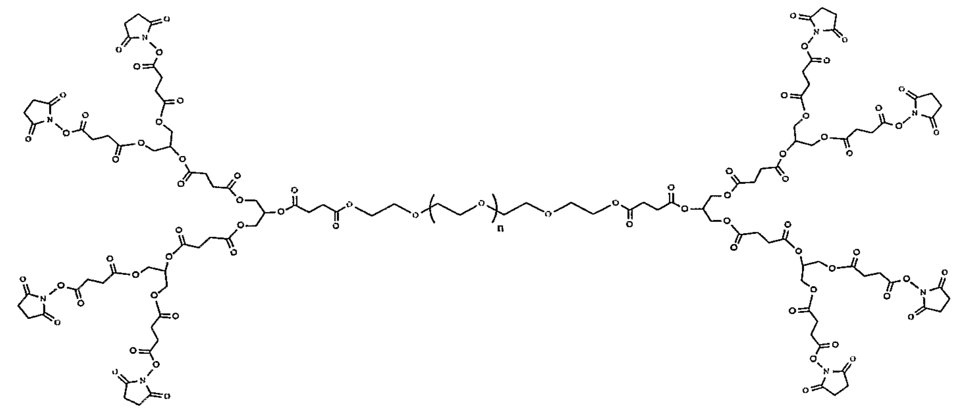


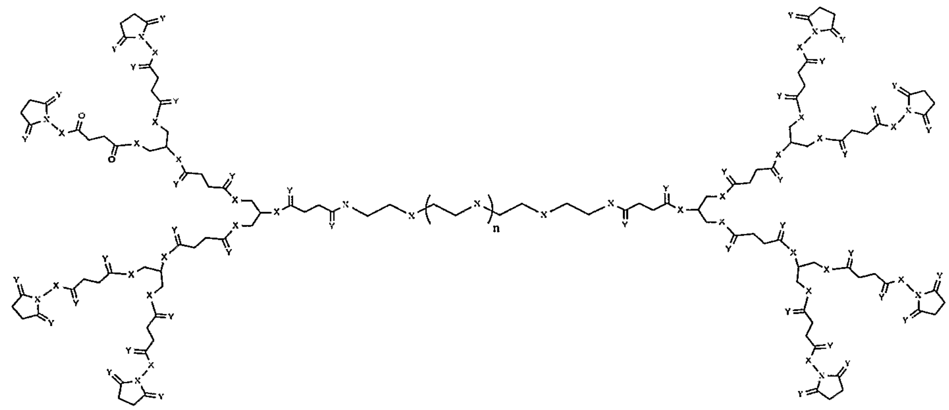












Sterilization Procedures

A variety of procedures are known in the art for sterilizing a chemical composition. Sterilization may be accomplished by chemical, physical, or irradiation techniques. Examples of chemical methods include exposure to ethylene oxide or hydrogen peroxide vapor. Examples of physical methods include sterilization by heat (dry or moist), retort canning, and filtration. The British Pharmacopoeia recommends heating at a minimum of 160 °C for not less than 2 hours, a minimum of 170 °C for not less than 1 hour and a minimum of 180 °C for not less than 30 minutes for effective sterilization. For examples of heat sterilization, see U.S. Patent 6,136,326, which is hereby incorporated by reference. Passing the chemical composition through a membrane can be used to sterilize a composition. For example, the composition is filtered through a small pore filter such as a 0.22 micron filter which comprises material inert to the composition being filtered. In

certain instances, the filtration is conducted in a Class 100,000 or better clean room. Examples of irradiation methods include gamma irradiation, electron beam irradiation, microwave irradiation, and irradiation using visible light. One preferred method is electron beam irradiation, as described in U.S. Patents 6,743,858; 6,248,800; and 6,143,805, each of which is hereby incorporated by reference.

There are several sources for electron beam irradiation. The two main groups of electron beam accelerators are: (1) a Dynamitron, which uses an insulated core transformer, and (2) radio frequency (RF) linear accelerators (linacs). The Dynamitron is a particle accelerator (4.5 MeV) designed to impart energy to electrons. The high energy electrons are generated and accelerated by the electrostatic fields of the accelerator electrodes arranged within the length of the glass-insulated beam tube (acceleration tube). These electrons, traveling through an extension of the evacuation beam tube and beam transport (drift pipe) are subjected to a magnet deflection system in order to produce a "scanned" beam, prior to leaving the vacuum enclosure through a beam window. The dose can be adjusted with the control of the percent scan, the beam current, and the conveyor speed. In certain instances, the electron-beam radiation employed may be maintained at an initial fluence of at least about 2 μCurie/cm^2, at least about 5 μCurie/cm^2, at least about 8 μCurie/cm^2, or at least about 10 μCurie/cm^2. In certain instances, the electron-beam radiation employed has an initial fluence of from about 2 to about 25 μCurie/cm^2. In certain instances, the electron-beam dosage is from about 5 to 50 kGray, or from about 15 to about 20 kGray with the specific dosage being selected relative to the density of material being subjected to electron-beam radiation as well as the amount of bioburden estimated to be therein. Such factors are well within the skill of the art.

The composition to be sterilized may be in any type of at least partially electron beam permeable container such as glass or plastic. In embodiments of the present invention, the container may be sealed or have an opening. Examples of glass containers include ampules, vials, syringes, pipettes, applicators, and the like. The penetration of electron beam irradiation is a function of the packaging. If there is not enough penetration from the side of a stationary electron beam, the container may be flipped or rotated to achieve adequate penetration. Alternatively, the electron beam source can be moved about a stationary package. In order to determine the dose distribution and dose penetration in product load, a dose map can be performed. This will identify the minimum and maximum dose zone within a product.

Procedures for sterilization using visible light are described in U.S. Patent 6,579,916, which is hereby incorporated by reference. The visible light for sterilization can be generated using any conventional generator of sufficient power and breadth of wavelength to effect sterilization. Generators are commercially available under the tradename PureBright® in-line sterilization systems from PurePulse Technologies, Inc. 4241 Ponderosa Ave, San Diego, Calif. 92123, USA. The PureBright® in-line sterilization system employs visible light to sterilize clear liquids at an intensity approximately 90000 times greater than surface sunlight. If the amount of UV light penetration is of concern, conventional UV absorbing materials can be used to filter out the UV light.

In a preferred embodiment, the composition is sterilized to provide a Sterility Assurance Level (SAL) of at least about 10^{-3}. The Sterility Assurance Level measurement standard is described, for example, in ISO/CD 14937, the entire disclosure of which is incorporated herein by reference. In certain embodiments, the Sterility Assurance Level may be at least about 10^{-4}, at least about 10^{-5}, or at least about 10^{-6}.

Delivery Systems

The materials used to form the sealant of the present invention may be delivered to the wound of a patient using a large number of known delivery devices. For example, the delivery system may be a single-barrel syringe system. In certain instances, the single-barrel syringe is a double acting, single-barrel syringe system as displayed in Figure 10. In certain situations, a double- or multi-barrel syringe system, as displayed in Figure 11, may be preferable. In instances where the polymerizable dendrimer is mixed with a polymerization agent prior to delivering the solution to the wound of a patient, a delivery device that flows two or more streams of liquid in a mixing chamber may be preferable. Alternatively, a delivery device that mixes two solids and two liquids and then separately flows these streams of liquid to a mixing chamber may be advantageous. In certain instances, a delivery system is used to deliver the sealant-forming materials to the wound of a patient, wherein at least two dry, reactive components are stored together in a dry state and introduced into a liquid component(s) at the time of use to form a mixture that forms a hydrogel.

In certain instances, it may be advantageous the mix the components used to form the hydrogel by a tortuous path mixing element. For example, the two components could

be mixed (without gelation) prior to applying the mixture to a patient. The pH of the mixing solution may be adjusted in order to slow or prevent crosslinking of hydrogel components. Once the components used to form the hydrogel are mixed, the resultant solution may be contacted with a frit or resin designed to raise or lower the pH to a level suitable for crosslinking.

For example, PEG-SPA and Lys3Cys4 could be mixed during packaging and dissolved prior to use in a buffer designed to provide a solution with a pH of about 6. The solution is mixed, and then the solution is contacted with a resin embedded in the delivery device. The resin would raise the pH to about 7 for initiate crosslinking.

Pharmaceutical Agents

A large number of pharmaceutical agents are known in the art and are amenable for use in the pharmaceutical compositions of the invention. The term "pharmaceutical agent" includes without limitation, medicaments; vitamins; mineral supplements; substances used for the treatment, prevention, diagnosis, cure or mitigation of disease or illness; or substances which affect the structure or function of the body; or pro-drugs, which become biologically active or more active after they have been placed in a predetermined physiological environment.

Non-limiting examples of broad categories of useful pharmaceutical agents include the following therapeutic categories: anabolic agents, antacids, anti-asthmatic agents, anti-cholesterolemic and anti-lipid agents, anti-coagulants, anti-convulsants, anti-diarrheals, anti-emetics, anti-infective agents, anti-inflammatory agents, anti-manic agents, anti-nauseants, anti-neoplastic agents, anti-obesity agents, anti-pyretic and analgesic agents, anti-spasmodic agents, anti-thrombotic agents, anti-uricemic agents, anti-anginal agents, antihistamines, anti-tussives, appetite suppressants, biologicals, cerebral dilators, coronary dilators, decongestants, diuretics, diagnostic agents, erythropoietic agents, expectorants, gastrointestinal sedatives, hyperglycemic agents, hypnotics, hypoglycemic agents, ion exchange resins, laxatives, mineral supplements, mucolytic agents, neuromuscular drugs, peripheral vasodilators, psychotropics, sedatives, stimulants, thyroid and anti-thyroid agents, uterine relaxants, vitamins, and prodrugs.

More specifically, non-limiting examples of useful pharmaceutical agents include the following therapeutic categories: analgesics, such as nonsteroidal anti-inflammatory

drugs, opiate agonists and salicylates; antihistamines, such as H_1-blockers and H_2 -blockers; anti-infective agents, such as anthelmintics, antianaerobics, antibiotics, aminoglycoside antibiotics, antifungal antibiotics, cephalosporin antibiotics, macrolide antibiotics, miscellaneous beta-lactam antibiotics, penicillin antibiotics, quinolone antibiotics, sulfonamide antibiotics, tetracycline antibiotics, antimycobacterials, antituberculosis antimycobacterials, antiprotozoals, antimalarial antiprotozoals, antiviral agents, anti-retroviral agents, scabicides, and urinary anti-infectives; antineoplastic agents, such as alkylating agents, nitrogen mustard aklylating agents, nitrosourea alkylating agents, antimetabolites, purine analog antimetabolites, pyrimidine analog antimetabolites, hormonal antineoplastics, natural antineoplastics, antibiotic natural antineoplastics, and vinca alkaloid natural antineoplastics; autonomic agents, such as anticholinergics, antimuscarinic anticholinergics, ergot alkaloids, parasympathomimetics, cholinergic agonist parasympathomimetics, cholinesterase inhibitor para-sympathomimetics, sympatholytics, alpha-blocker sympatholytics, beta-blocker sympatholytics, sympathomimetics, and adrenergic agonist sympathomimetics; cardiovascular agents, such as antianginals, beta-blocker antianginals, calcium-channel blocker antianginals, nitrate antianginals, antiarrhythmics, cardiac glycoside antiarrhythmics, class I antiarrhythmics, class II antiarrhythmics, class III antiarrhythmics, class IV antiarrhythmics, antihypertensive agents, alpha-blocker antihypertensives, angiotensin-converting enzyme inhibitor (ACE inhibitor) antihypertensives, beta-blocker antihypertensives, calcium-channel blocker antihypertensives, central-acting adrenergic antihypertensives, diuretic antihypertensive agents, peripheral vasodilator antihypertensives, antilipemics, bile acid sequestrant antilipemics, HMG-CoA reductase inhibitor antilipemics, inotropes, cardiac glycoside inotropes, and thrombolytic agents; dermatological agents, such as antihistamines, anti-inflammatory agents, corticosteroid anti-inflammatory agents, antipruritics/local anesthetics, topical anti-infectives, antifungal topical anti-infectives, antiviral topical anti-infectives, and topical antineoplastics; electrolytic and renal agents, such as acidifying agents, alkalinizing agents, diuretics, carbonic anhydrase inhibitor diuretics, loop diuretics, osmotic diuretics, potassium-sparing diuretics, thiazide diuretics, electrolyte replacements, and uricosuric agents; enzymes, such as pancreatic enzymes and thrombolytic enzymes; gastrointestinal agents, such as antidiarrheals, antiemetics, gastrointestinal anti-inflammatory agents, salicylate gastrointestinal anti-inflammatory agents, antacid anti-ulcer agents, gastric acid-pump inhibitor anti-ulcer agents, gastric mucosal anti-ulcer agents, H_2 -

blocker anti-ulcer agents, cholelitholytic agents, digestants, emetics, laxatives and stool softeners, and prokinetic agents; general anesthetics, such as inhalation anesthetics, halogenated inhalation anesthetics, intravenous anesthetics, barbiturate intravenous anesthetics, benzodiazepine intravenous anesthetics, and opiate agonist intravenous anesthetics; hematological agents, such as antianemia agents, hematopoietic antianemia agents, coagulation agents, anticoagulants, hemostatic coagulation agents, platelet inhibitor coagulation agents, thrombolytic enzyme coagulation agents, and plasma volume expanders; hormones and hormone modifiers, such as abortifacients, adrenal agents, corticosteroid adrenal agents, androgens, anti-androgens, antidiabetic agents, sulfonylurea antidiabetic agents, antihypoglycemic agents, oral contraceptives, progestin contraceptives, estrogens, fertility agents, oxytocics, parathyroid agents, pituitary hormones, progestins, antithyroid agents, thyroid hormones, and tocolytics; immunobiologic agents, such as immunoglobulins, immunosuppressives, toxoids, and vaccines; local anesthetics, such as amide local anesthetics and ester local anesthetics; musculoskeletal agents, such as anti-gout anti-inflammatory agents, corticosteroid anti-inflammatory agents, gold compound anti-inflammatory agents, immuno-suppressive anti-inflammatory agents, nonsteroidal anti-inflammatory drugs (NSAIDs), salicylate anti-inflammatory agents, skeletal muscle relaxants, neuromuscular blocker skeletal muscle relaxants, and reverse neuromuscular blocker skeletal muscle relaxants; neurological agents, such as anticonvulsants, barbiturate anticonvulsants, benzodiazepine anticonvulsants, anti-migraine agents, anti-parkinsonian agents, anti-vertigo agents, opiate agonists, and opiate antagonists; ophthalmic agents, such as anti-glaucoma agents, beta-blocker anti-gluacoma agents, miotic anti-glaucoma agents, mydriatics, adrenergic agonist mydriatics, antimuscarinic mydriatics, ophthalmic anesthetics, ophthalmic anti-infectives, ophthalmic aminoglycoside anti-infectives, ophthalmic macrolide anti-infectives, ophthalmic quinolone anti-infectives, ophthalmic sulfonamide anti-infectives, ophthalmic tetracycline anti-infectives, ophthalmic anti-inflammatory agents, ophthalmic corticosteroid anti-inflammatory agents, and ophthalmic nonsteroidal anti-inflammatory drugs (NSAIDs); psychotropic agents, such as antidepressants, heterocyclic antidepressants, monoamine oxidase inhibitors (MAOIs), selective serotonin re-uptake inhibitors (SSRIs), tricyclic antidepressants, antimanics, antipsychotics, phenothiazine antipsychotics, anxiolytics, sedatives, and hypnotics, barbiturate sedatives and hypnotics, benzodiazepine anxiolytics, sedatives, and hypnotics, and psychostimulants; respiratory agents, such as antitussives, bronchodilators, adrenergic

agonist bronchodilators, antimuscarinic bronchodilators, expectorants, mucolytic agents, respiratory anti-inflammatory agents, and respiratory corticosteroid anti-inflammatory agents; toxicology agents, such as antidotes, heavy metal antagonists/chelating agents, substance abuse agents, deterrent substance abuse agents, and withdrawal substance abuse agents; minerals; and vitamins, such as vitamin A, vitamin B, vitamin C, vitamin D, vitamin E, and vitamin K.

Preferred classes of useful pharmaceutical agents from the above categories include: (1) nonsteroidal anti-inflammatory drugs (NSAIDs) analgesics, such as diclofenac, ibuprofen, ketoprofen, and naproxen; (2) opiate agonist analgesics, such as codeine, fentanyl, hydromorphone, and morphine; (3) salicylate analgesics, such as aspirin (ASA) (enteric coated ASA); (4) H_1 -blocker antihistamines, such as clemastine and terfenadine; (5) H_2 -blocker antihistamines, such as cimetidine, famotidine, nizadine, and ranitidine; (6) anti-infective agents, such as mupirocin; (7) antianaerobic anti-infectives, such as chloramphenicol and clindamycin; (8) antifungal antibiotic anti-infectives, such as amphotericin b, clotrimazole, fluconazole, and ketoconazole; (9) macrolide antibiotic anti-infectives, such as azithromycin and erythromycin; (10) miscellaneous beta-lactam antibiotic anti-infectives, such as aztreonam and imipenem; (11) penicillin antibiotic anti-infectives, such as nafcillin, oxacillin, penicillin G, and penicillin V; (12) quinolone antibiotic anti-infectives, such as ciprofloxacin and norfloxacin; (13) tetracycline antibiotic anti-infectives, such as doxycycline, minocycline, and tetracycline; (14) antituberculosis antimycobacterial anti-infectives such as isoniazid (INH), and rifampin; (15) antiprotozoal anti-infectives, such as atovaquone and dapsone; (16) antimalarial antiprotozoal anti-infectives, such as chloroquine and pyrimethamine; (17) anti-retroviral anti-infectives, such as ritonavir and zidovudine; (18) antiviral anti-infective agents, such as acyclovir, ganciclovir, interferon alfa, and rimantadine; (19) alkylating antineoplastic agents, such as carboplatin and cisplatin; (20) nitrosourea alkylating antineoplastic agents, such as carmustine (BCNU); (21) antimetabolite antineoplastic agents, such as methotrexate; (22) pyrimidine analog antimetabolite antineoplastic agents, such as fluorouracil (5-FU) and gemcitabine; (23) hormonal antineoplastics, such as goserelin, leuprolide, and tamoxifen; (24) natural antineoplastics, such as aldesleukin, interleukin-2, docetaxel, etoposide (VP-16), interferon alfa, paclitaxel, and tretinoin (ATRA); (25) antibiotic natural antineoplastics, such as bleomycin, dactinomycin, daunorubicin, doxorubicin, and mitomycin; (26) vinca alkaloid natural antineoplastics, such as vinblastine and vincristine; (27) autonomic agents,

such as nicotine; (28) anticholinergic autonomic agents, such as benztropine and trihexyphenidyl; (29) antimuscarinic anticholinergic autonomic agents, such as atropine and oxybutynin; (30) ergot alkaloid autonomic agents, such as bromocriptine; (31) cholinergic agonist parasympathomimetics, such as pilocarpine; (32) cholinesterase inhibitor parasympathomimetics, such as pyridostigmine; (33) alpha-blocker sympatholytics, such as prazosin; (34) beta-blocker sympatholytics, such as atenolol; (35) adrenergic agonist sympathomimetics, such as albuterol and dobutamine; (36) cardiovascular agents, such as aspirin (ASA) (enteric coated ASA); (37) beta-blocker antianginals, such as atenolol and propranolol; (38) calcium-channel blocker antianginals, such as nifedipine and verapamil; (39) nitrate antianginals, such as isosorbide dinitrate (ISDN); (40) cardiac glycoside antiarrhythmics, such as digoxin; (41) class I anti-arrhythmics, such as lidocaine, mexiletine, phenytoin, procainamide, and quinidine; (42) class II antiarrhythmics, such as atenolol, metoprolol, propranolol, and timolol; (43) class III antiarrhythmics, such as amiodarone; (44) class IV antiarrhythmics, such as diltiazem and verapamil; (45) .alpha.-blocker antihypertensives, such as prazosin; (46) angiotensin-converting enzyme inhibitor (ACE inhibitor) antihypertensives, such as captopril and enalapril; (47) .beta.-blocker antihypertensives, such as atenolol, metoprolol, nadolol, and propanolol; (48) calcium-channel blocker antihypertensive agents, such as diltiazem and nifedipine; (49) central-acting adrenergic antihypertensives, such as clonidine and methyldopa; (50) diurectic antihypertensive agents, such as amiloride, furosemide, hydrochlorothiazide (HCTZ), and spironolactone; (51) peripheral vasodilator antihypertensives, such as hydralazine and minoxidil; (52) antilipemics, such as gemfibrozil and probucol; (53) bile acid sequestrant antilipemics, such as cholestyramine; (54) HMG-CoA reductase inhibitor antilipemics, such as lovastatin and pravastatin; (55) inotropes, such as amrinone, dobutamine, and dopamine; (56) cardiac glycoside inotropes, such as digoxin; (57) thrombolytic agents, such as alteplase (TPA), anistreplase, streptokinase, and urokinase; (58) dermatological agents, such as colchicine, isotretinoin, methotrexate, minoxidil, tretinoin (ATRA); (59) dermatological corticosteroid anti-inflammatory agents, such as betamethasone and dexamethasone; (60) antifungal topical anti-infectives, such as amphotericin B, clotrimazole, miconazole, and nystatin; (61) antiviral topical anti-infectives, such as acyclovir; (62) topical antineoplastics, such as fluorouracil (5-FU); (63) electrolytic and renal agents, such as lactulose; (64) loop diuretics, such as furosemide; (65) potassium-sparing diuretics, such as triamterene; (66) thiazide diuretics, such as hydro-chlorothiazide

(HCTZ); (67) uricosuric agents, such as probenecid; (68) enzymes such as RNase and DNase; (69) thrombolytic enzymes, such as alteplase, anistreplase, streptokinase and urokinase; (70) antiemetics, such as prochlorperazine; (71) salicylate gastrointestinal anti-inflammatory agents, such as sulfasalazine; (72) gastric acid-pump inhibitor anti-ulcer agents, such as omeprazole; (73) H.sub.2 -blocker anti-ulcer agents, such as cimetidine, famotidine, nizatidine, and ranitidine; (74) digestants, such as pancrelipase; (75) prokinetic agents, such as erythromycin; (76) opiate agonist intravenous anesthetics such as fentanyl; (77) hematopoietic antianemia agents, such as erythropoietin, filgrastim (G-CSF), and sargramostim (GM-CSF); (78) coagulation agents, such as antihemophilic factors 1-10 (AHF 1-10); (79) anticoagulants, such as warfarin; (80) thrombolytic enzyme coagulation agents, such as alteplase, anistreplase, streptokinase and urokinase; (81) hormones and hormone modifiers, such as bromocriptine; (82) abortifacients, such as methotrexate; (83) antidiabetic agents, such as insulin; (84) oral contraceptives, such as estrogen and progestin; (85) progestin contraceptives, such as levonorgestrel and norgestrel; (86) estrogens such as conjugated estrogens, diethylstilbestrol (DES), estrogen (estradiol, estrone, and estropipate); (87) fertility agents, such as clomiphene, human chorionic gonadatropin (HCG), and menotropins; (88) parathyroid agents such as calcitonin; (89) pituitary hormones, such as desmopressin, goserelin, oxytocin, and vasopressin (ADH); (90) progestins, such as medroxyprogesterone, norethindrone, and progesterone; (91) thyroid hormones, such as levothyroxine; (92) immunobiologic agents, such as interferon beta-1b and interferon gamma-1b; (93) immunoglobulins, such as immune globulin IM, IMIG, IGIM and immune globulin IV, IVIG, IGIV; (94) amide local anesthetics, such as lidocaine; (95) ester local anesthetics, such as benzocaine and procaine; (96) musculoskeletal corticosteroid anti-inflammatory agents, such as beclomethasone, betamethasone, cortisone, dexamethasone, hydrocortisone, and prednisone; (97) musculoskeletal anti-inflammatory immunosuppressives, such as azathioprine, cyclophosphamide, and methotrexate; (98) musculoskeletal nonsteroidal anti-inflammatory drugs (NSAIDs), such as diclofenac, ibuprofen, ketoprofen, ketorlac, and naproxen; (99) skeletal muscle relaxants, such as baclofen, cyclobenzaprine, and diazepam; (100) reverse neuromuscular blocker skeletal muscle relaxants, such as pyridostigmine; (101) neurological agents, such as nimodipine, riluzole, tacrine and ticlopidine; (102) anticonvulsants, such as carbamazepine, gabapentin, lamotrigine, phenytoin, and valproic acid; (103) barbiturate anticonvulsants, such as phenobarbital and primidone; (104)

benzodiazepine anticonvulsants, such as clonazepam, diazepam, and lorazepam; (105) anti-parkisonian agents, such as bromocriptine, levodopa, carbidopa, and pergolide; (106) anti-vertigo agents, such as meclizine; (107) opiate agonists, such as codeine, fentanyl, hydromorphone, methadone, and morphine; (108) opiate antagonists, such as naloxone; (109) .beta.-blocker anti-glaucoma agents, such as timolol; (110) miotic anti-glaucoma agents, such as pilocarpine; (111) ophthalmic aminoglycoside antiinfectives, such as gentamicin, neomycin, and tobramycin; (112) ophthalmic quinolone anti-infectives, such as ciprofloxacin, norfloxacin, and ofloxacin; (113) ophthalmic corticosteroid anti-inflammatory agents, such as dexamethasone and prednisolone; (114) ophthalmic nonsteroidal anti-inflammatory drugs (NSAIDs), such as diclofenac; (115) antipsychotics, such as clozapine, haloperidol, and risperidone; (116) benzodiazepine anxiolytics, sedatives and hypnotics, such as clonazepam, diazepam, lorazepam, oxazepam, and prazepam; (117) psychostimulants, such as methylphenidate and pemoline; (118) antitussives, such as codeine; (119) bronchodilators, such as theophylline; (120) adrenergic agonist bronchodilators, such as albuterol; (121) respiratory corticosteroid anti-inflammatory agents, such as dexamethasone; (122) antidotes, such as flumazenil and naloxone; (123) heavy metal antagonists/chelating agents, such as penicillamine; (124) deterrent substance abuse agents, such as disulfiram, naltrexone, and nicotine; (125) withdrawal substance abuse agents, such as bromocriptine; (126) minerals, such as iron, calcium, and magnesium; (127) vitamin B compounds, such as cyanocobalamin (vitamin B.sub.12) and niacin (vitamin B.sub.3); (128) vitamin C compounds, such as ascorbic acid; and (129) vitamin D compounds, such as calcitriol.

In addition to the foregoing, the following less common drugs may also be used: chlorhexidine; estradiol cypionate in oil; estradiol valerate in oil; flurbiprofen; flurbiprofen sodium; ivermectin; levodopa; nafarelin; and somatropin. Further, the following drugs may also be used: recombinant beta-glucan; bovine immunoglobulin concentrate; bovine superoxide dismutase; the formulation comprising fluorouracil, epinephrine, and bovine collagen; recombinant hirudin (r-Hir), HIV-1 immunogen; human anti-TAC antibody; recombinant human growth hormone (r-hGH); recombinant human hemoglobin (r-Hb); recombinant human mecasermin (r-IGF-1); recombinant interferon beta-1a; lenograstim (G-CSF); olanzapine; recombinant thyroid stimulating hormone (r-TSH); and topotecan.

Further still, the following intravenous products may be used: acyclovir sodium; aldesleukin; atenolol; bleomycin sulfate, human calcitonin; salmon calcitonin; carboplatin;

carmustine; dactinomycin, daunorubicin HCl; docetaxel; doxorubicin HCl; epoetin alfa; etoposide (VP-16); fluorouracil (5-FU); ganciclovir sodium; gentamicin sulfate; interferon alfa; leuprolide acetate; meperidine HCl; methadone HCl; methotrexate sodium; paclitaxel; ranitidine HCl; vinblastin sulfate; and zidovudine (AZT).

Further specific examples of useful pharmaceutical agents from the above categories include: (a) anti-neoplastics such as androgen inhibitors, antimetabolites, cytotoxic agents, and immunomodulators; (b) anti-tussives such as dextromethorphan, dextromethorphan hydrobromide, noscapine, carbetapentane citrate, and chlorphedianol hydrochloride; (c) antihistamines such as chlorpheniramine maleate, phenindamine tartrate, pyrilamine maleate, doxylamine succinate, and phenyltoloxamine citrate; (d) decongestants such as phenylephrine hydrochloride, phenylpropanolamine hydrochloride, pseudoephedrine hydrochloride, and ephedrine; (e) various alkaloids such as codeine phosphate, codeine sulfate and morphine; (f) mineral supplements such as potassium chloride, zinc chloride, calcium carbonates, magnesium oxide, and other alkali metal and alkaline earth metal salts; (g) ion exchange resins such as cholestryramine; (h) anti-arrhythmics such as N-acetylprocainamide; (i) antipyretics and analgesics such as acetaminophen, aspirin and ibuprofen; (j) appetite suppressants such as phenyl-propanolamine hydrochloride or caffeine; (k) expectorants such as guaifenesin; (l) antacids such as aluminum hydroxide and magnesium hydroxide; (m) biologicals such as peptides, polypeptides, proteins and amino acids, hormones, interferons or cytokines, and other bioactive peptidic compounds, such as interleukins 1-18 including mutants and analogues, RNase, DNase, luteinizing hormone releasing hormone (LHRH) and analogues, gonadotropin releasing hormone (GnRH), transforming growth factor-.beta. (TGF-beta), fibroblast growth factor (FGF), tumor necrosis factor-alpha & beta (TNF-alpha & beta), nerve growth factor (NGF), growth hormone releasing factor (GHRF), epidermal growth factor (EGF), fibroblast growth factor homologous factor (FGFHF), hepatocyte growth factor (HGF), insulin growth factor (IGF), invasion inhibiting factor-2 (IIF-2), bone morphogenetic proteins 1-7 (BMP 1-7), somatostatin, thymosin-alpha-1, gamma-globulin, superoxide dismutase (SOD), complement factors, hGH, tPA, calcitonin, ANF, EPO and insulin; and (n) anti-infective agents such as antifungals, anti-virals, antiseptics and antibiotics.

Alternatively, the pharmaceutical agent may be a radiosensitizer, such as metoclopramide, sensamide or neusensamide (manufactured by Oxigene); profiromycin (made by Vion); RSR13 (made by Allos); Thymitaq (made by Agouron), etanidazole or

lobenguane (manufactured by Nycomed); gadolinium texaphrin (made by Pharmacyclics); BuDR/Broxine (made by NeoPharm); IPdR (made by Sparta); CR2412 (made by Cell Therapeutic); LIX (made by Terrapin); or the like. Preferably, the biologically active substance is selected from the group consisting of peptides, poly-peptides, proteins, amino acids, polysaccharides, growth factors, hormones, anti-angiogenesis factors, interferons or cytokines, and pro-drugs. In a particularly preferred embodiment, the biologically active substance is a therapeutic drug or pro-drug, most preferably a drug selected from the group consisting of chemotherapeutic agents and other anti-neoplastics such as paclitaxel, antibiotics, anti-virals, antifungals, anti-inflammatories, and anticoagulants.

The biologically active substances are used in amounts that are therapeutically effective. While the effective amount of a biologically active substance will depend on the particular material being used, amounts of the biologically active substance from about 1% to about 65% may be desirable. Lesser amounts may be used to achieve efficacious levels of treatment for certain biologically active substances.

Methods of the Invention Relating to Sealing a Wound

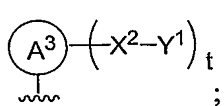
One aspect of the present invention relates to a method of sealing a wound of a patient, comprising the steps of:

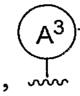
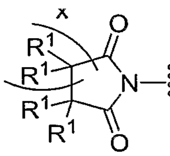
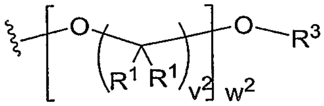
applying an effective amount of a sterilized dendrimeric compound of formula **I** to a wound of a patient, and exposing said dendrimeric compound to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is ultraviolet light, visible light, a compound of formula **II**, a compound of formula **III**, a compound of formula **IV**, or an oxidizing agent, wherein formula **I** is represented by:

$$A^1—X^1—B—X^1—A^2$$

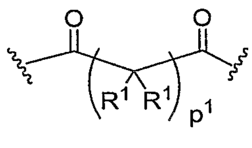
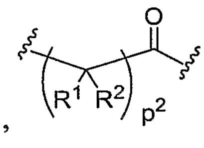
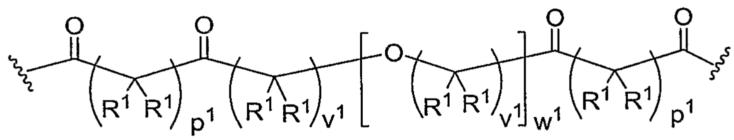
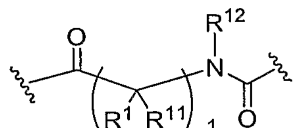
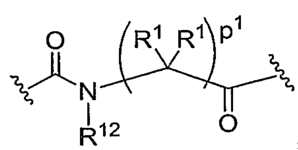
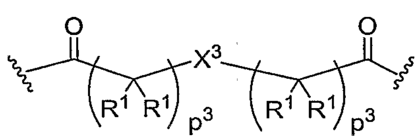
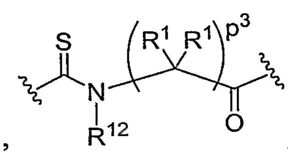
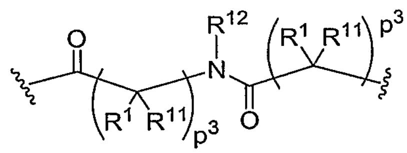
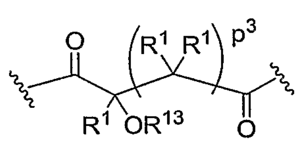
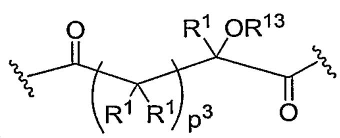
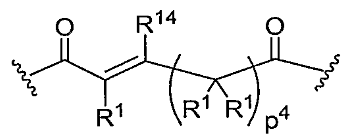
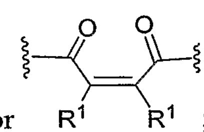
I

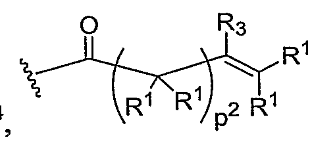
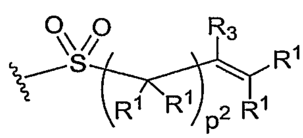
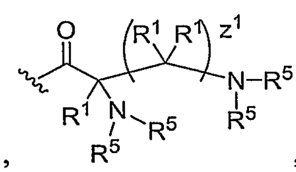
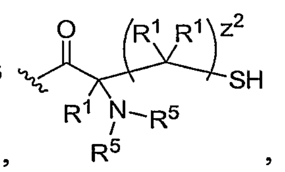
wherein

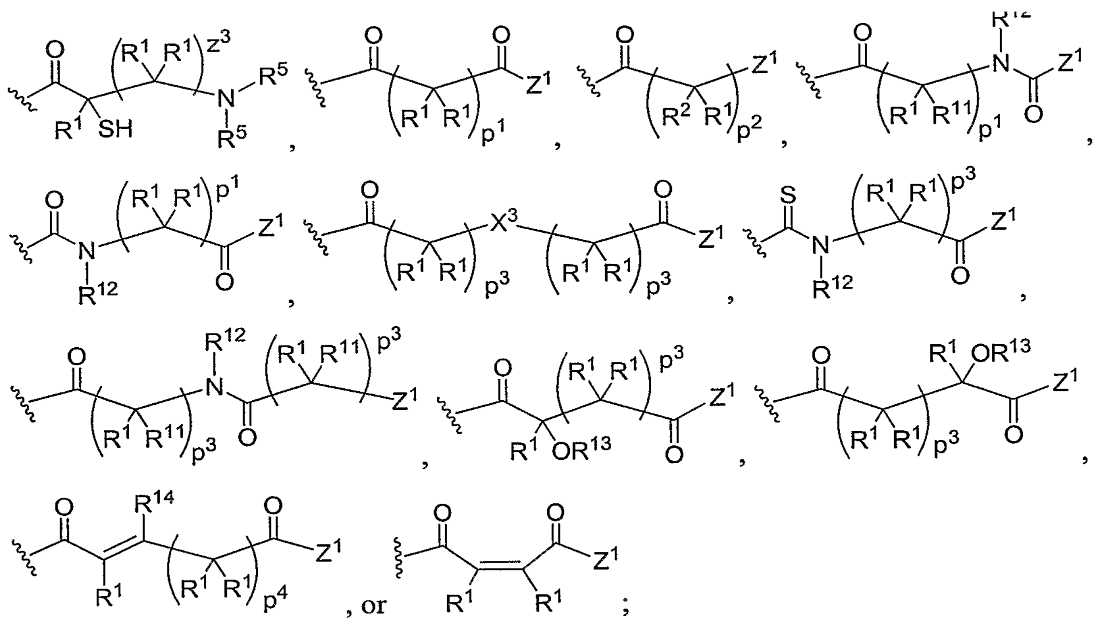
A^1 is  ;

A^2 is alkyl, aryl, aralkyl, $-Si(R^3)_3$, , , or ;

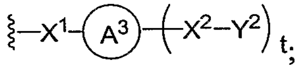
A^3 represents independently for each occurrence alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, heteroaryl, or aralkyl;

B is , , , , , , , , , , , or ;

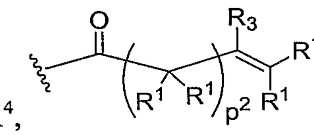
Y^1 represents independently for each occurrence R^4, A^4, , , , ,

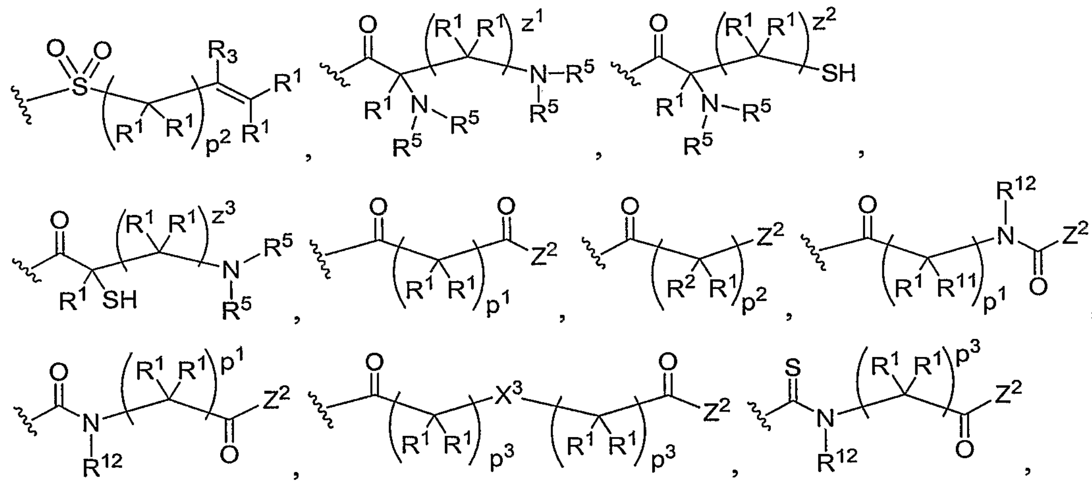


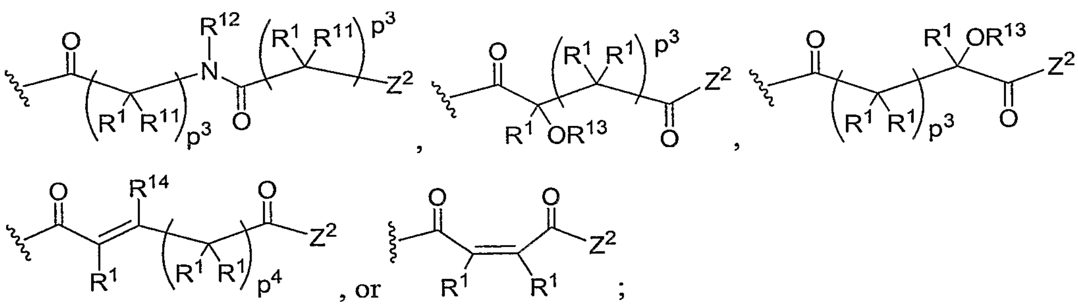
Z^1 represents independently for each occurrence $-X^1-R^4$, E, or



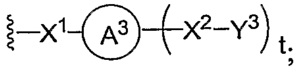
Y^2 represents independently for each occurrence R^5, A^4,



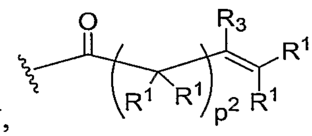


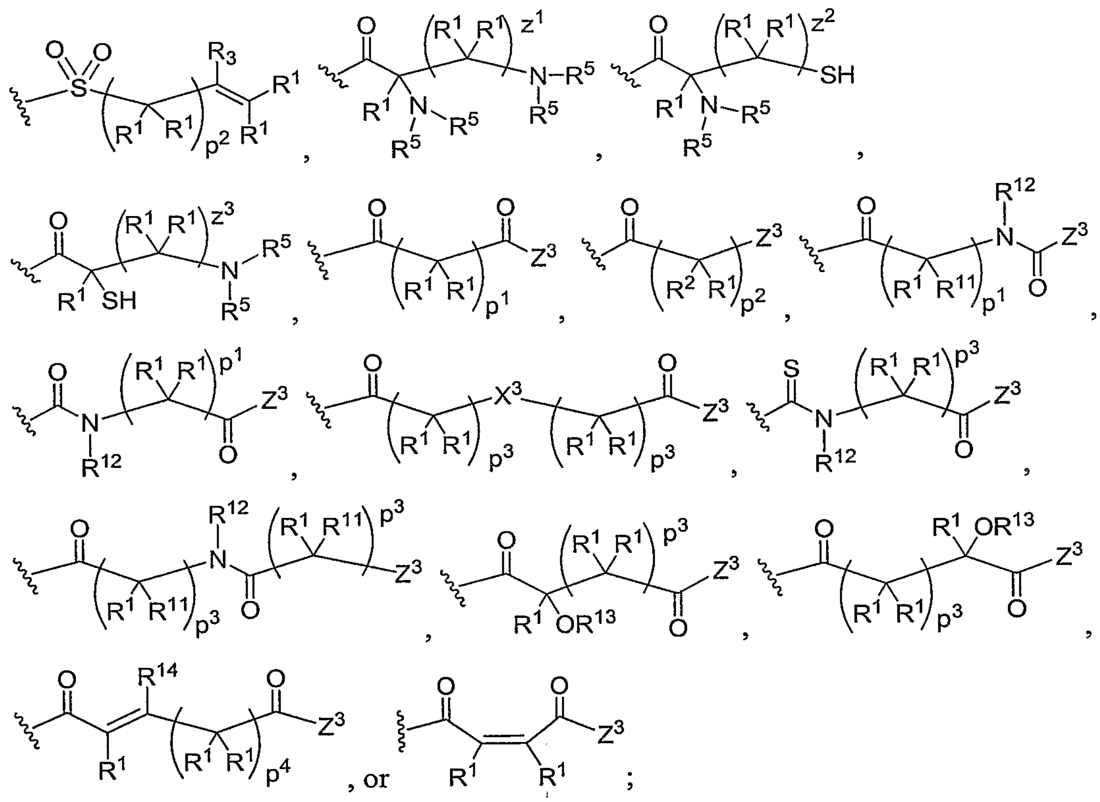


Z^2 represents independently for each occurrence $-X^1-R^5$, E, or

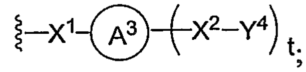


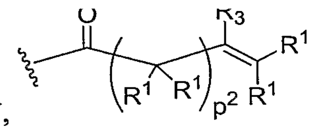
Y^3 represents independently for each occurrence R^6, A^4,

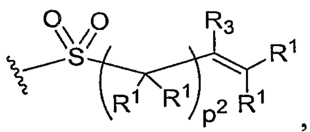
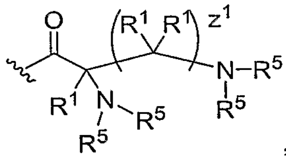
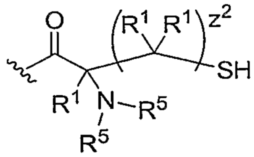


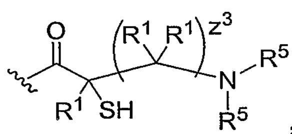
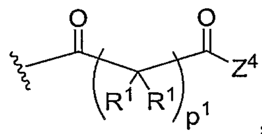
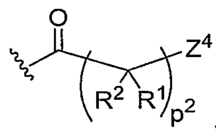
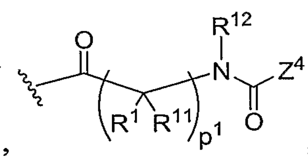


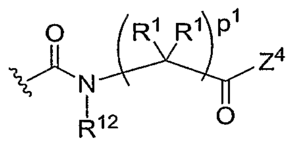
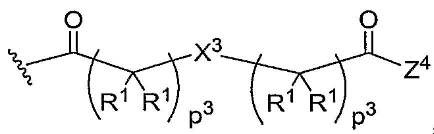
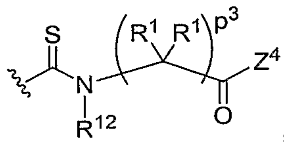
Z^3 represents independently for each occurrence $-X^1-R^6$, E, or

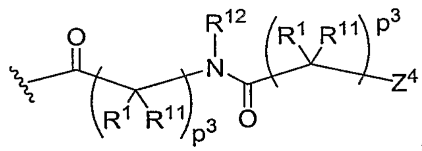
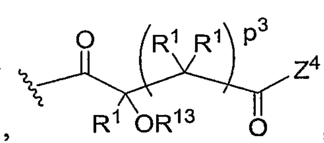
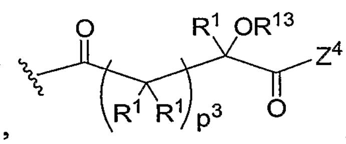


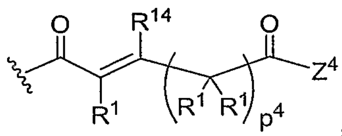
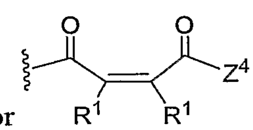
Y^4 represents independently for each occurrence R^7, A^4,  ,

 ,  ,  ,

 ,  ,  ,  ,

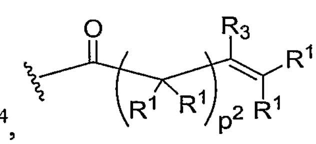
 ,  ,  ,

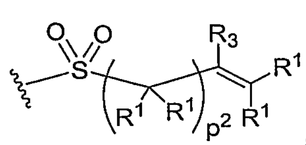
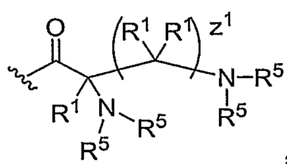
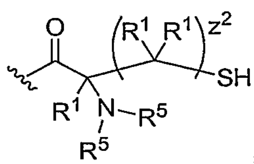
 ,  ,  ,

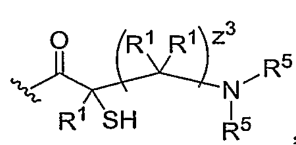
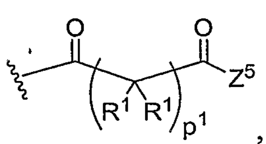
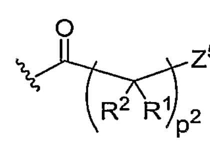
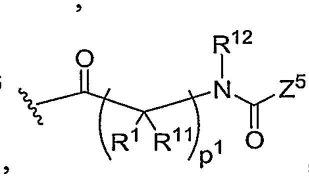
 , or  ;

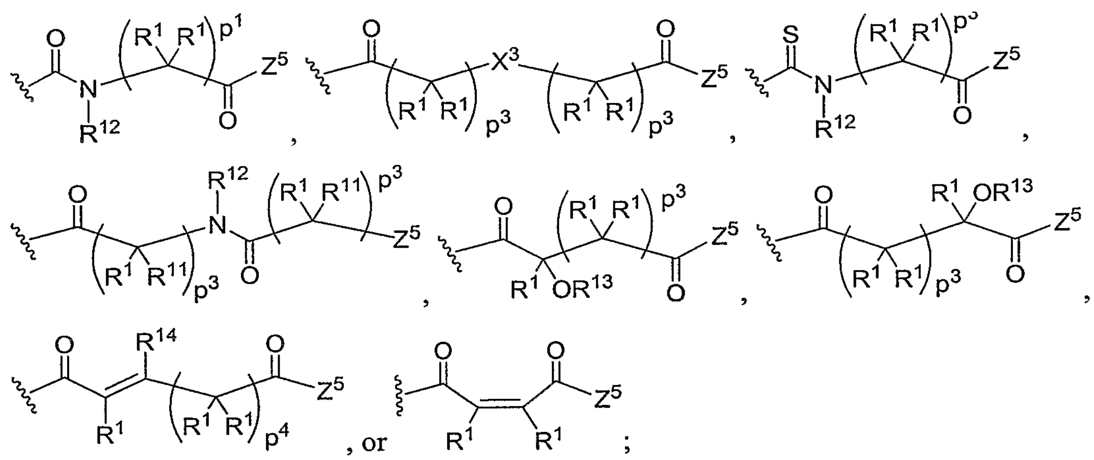
Z^4 represents independently for each occurrence $-X^1-R^7$, E, or

$-X^1-A^3-(X^2-Y^5)_t$;

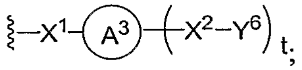
Y^5 represents independently for each occurrence R^8, A^4,  ,

 ,  ,  ,

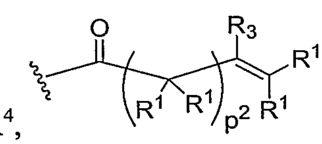
 ,  ,  ,  ,

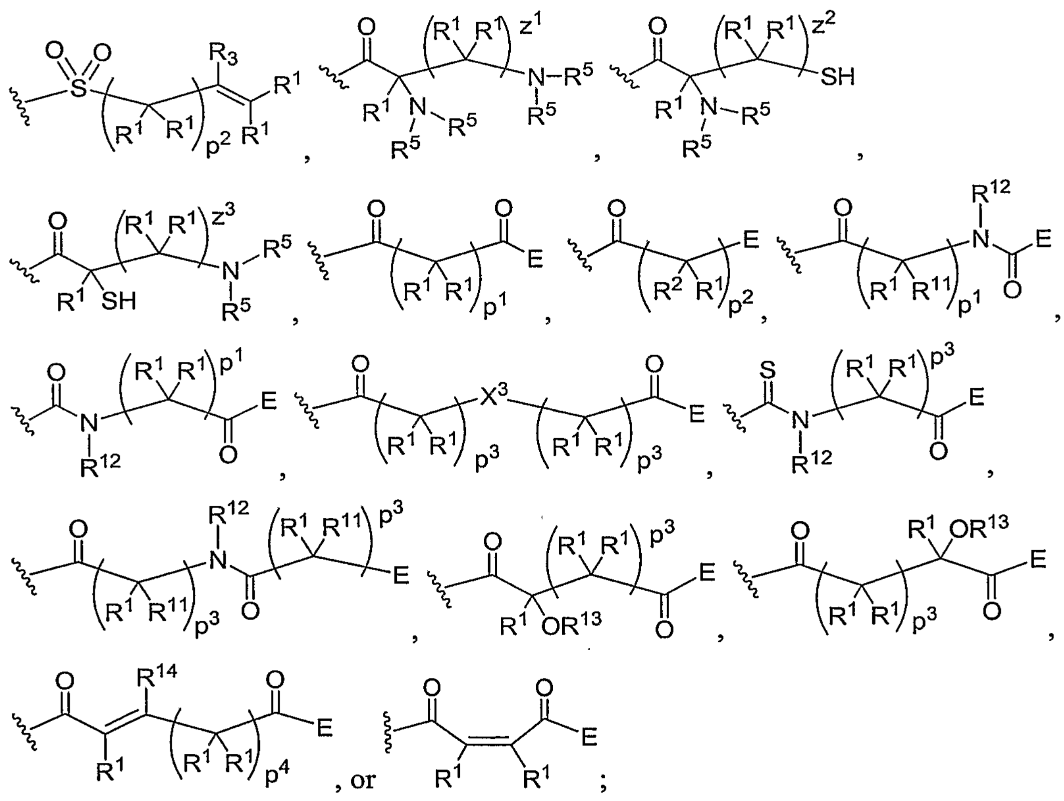


Z^5 represents independently for each occurrence $-X^1-R^8$, E, or



Y^6 represents independently for each occurrence R^9, A^4,





R^1 represents independently for each occurrence H, alkyl, or halogen;

R^2 represents independently for each occurrence H, alkyl, -OH, $-N(R^{10})_2$, -SH, hydroxyalkyl, or $-[C(R^1)_2]_dR^{16}$;

R^3 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^4, R^5, R^6, R^7, R^8, and R^9 are H;

R^{10} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{11} represents independently for each occurrence H, -OH, $-N(R^{10})_2$, -SH, alkyl, hydroxyalkyl, or $-[C(R^1)_2]_dR^{16}$;

R^{12} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{13} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{14} represents independently for each occurrence H, alkyl, or $-CO_2R^{10}$;

R^{15} represents independently for each occurrence H, alkyl, or $-OR^{10}$;

R^{16} represents independently for each occurrence phenyl, hydroxyphenyl, pyrrolidyl, imidazolyl, indolyl, $-N(R^{10})_2$, -SH, -S-alkyl, $-CO_2R^{10}$, $-C(O)N(R^{10})_2$, or $-C(NH_2)N(R^{10})_2$;

d represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

n represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

p^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7; or 8;

p^2 represents independently for each occurrence 0, 1, 2, 3, or 4;

p^3 represents independently for each occurrence 1, 2, or 3;

p^4 represents independently for each occurrence 0, 1, 2, or 3;

t represents independently for each occurrence 2, 3, 4, or 5 in accord with the rules of valence;

v^1 and v^2 each represent independently for each occurrence 2, 3, or 4;

w^1 and w^2 each represent independently for each occurrence an integer from about 5 to about 700, inclusive;

x is 1, 2, or 3;

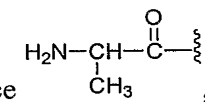
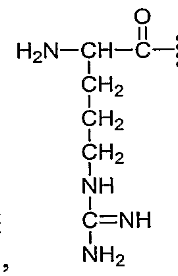
y is 0, 1, 2, 3, 4, or 5;

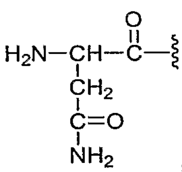
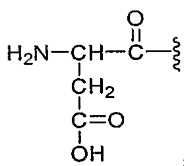
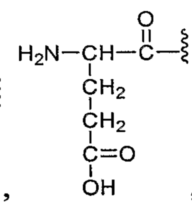
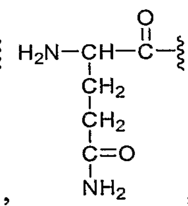
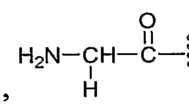
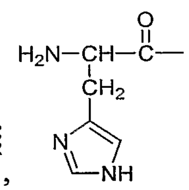
z^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

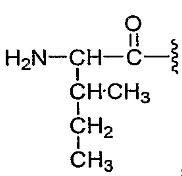
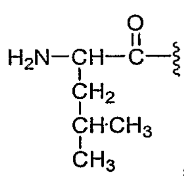
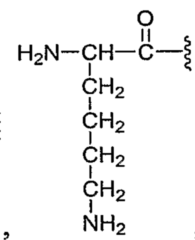
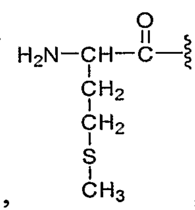
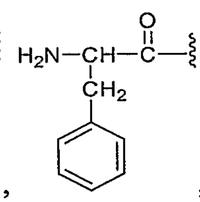
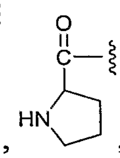
z^2 and z^3 each represent independently for each occurrence 1, 2, 3, 4, or 5;

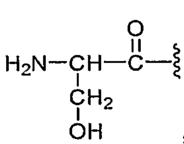
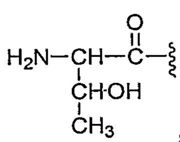
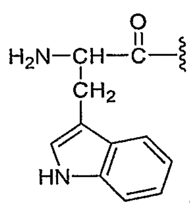
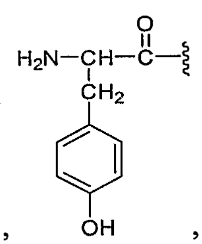
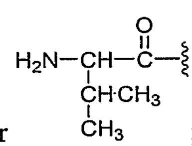
X^1 and X^2 each represent independently for each occurrence O or $-N(R^{10})-$;

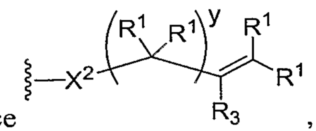
X^3 represents independently for each occurrence O, $N(R^{10})$, or $C(R^{15})(CO_2R^{10})$;

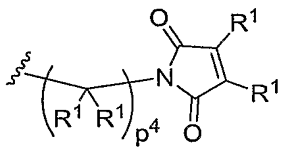
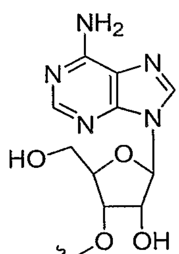
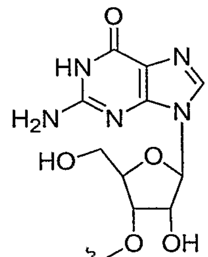
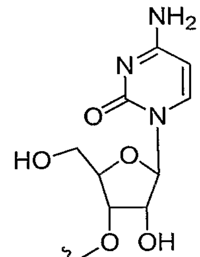
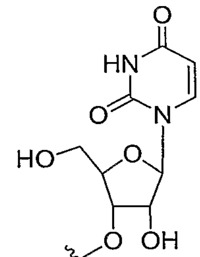
A^4 represents independently for each occurrence , ,

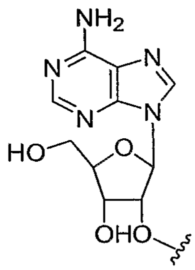
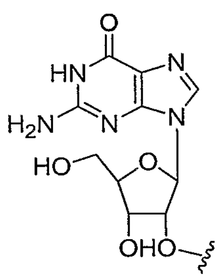
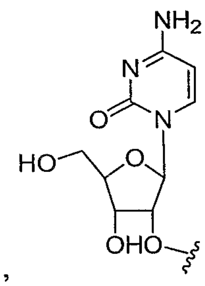
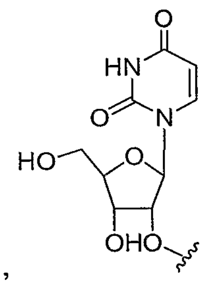
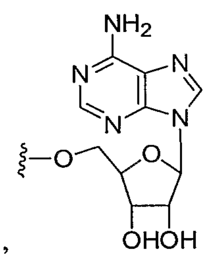
, , , , , ,

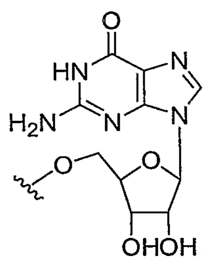
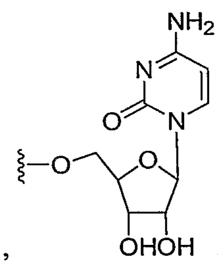
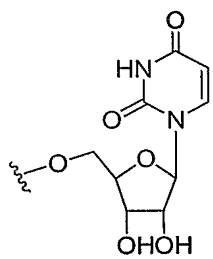
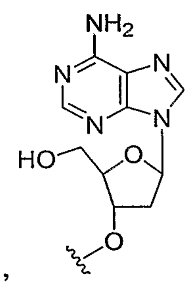
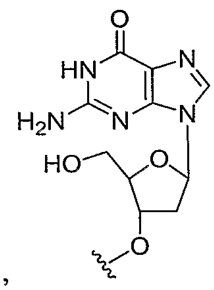
, , , , , ,

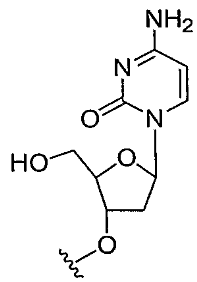
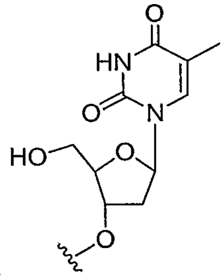
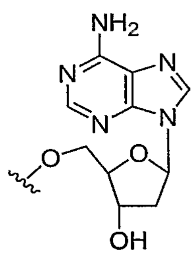
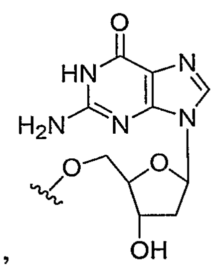
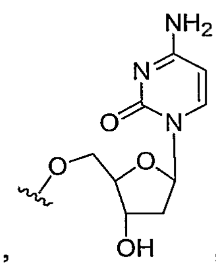
, , , , or ;

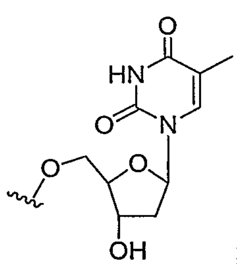
E represents independently for each occurrence ,

, , , , ,

, , , , ,

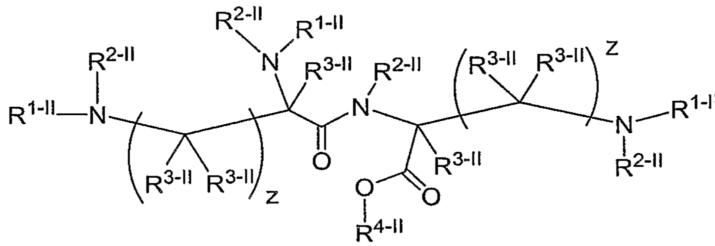
, , , , ,

, , , , , or

 ; and

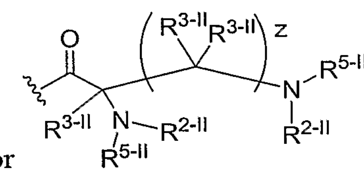
provided that R^4 only occurs once, R^5 only occurs once, R^6 only occurs once, R^7 only occurs once, R^8 only occurs once, and R^9 only occurs once;

said compound of formlua **II** is represented by:



II

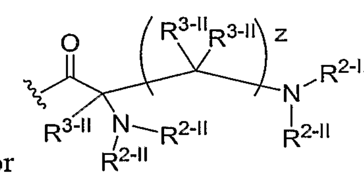
wherein

$R^{1\text{-}II}$ represents independently for each occurrence H or  ;

$R^{2\text{-}II}$ represents independently for each occurrence H or alkyl;

$R^{3\text{-}II}$ represents independently for each occurrence H, halogen, or alkyl;

$R^{4\text{-}II}$ represents independently for each occurrence alkyl, aryl, or aralkyl;

$R^{5\text{-}II}$ represents independently for each occurrence H or  ;

and

z represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8; and

said compound of formula **III** is represented by:

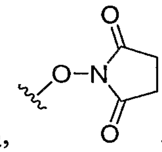
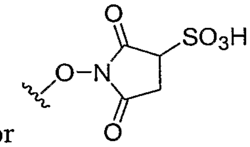
$$R^{1\text{-}III}—B^{1\text{-}III}—R^{1\text{-}III}$$

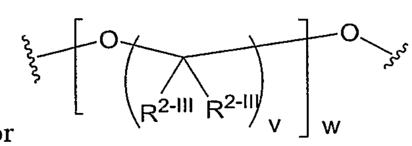
III

wherein

$R^{1\text{-}III}$ is $-(C(R^{2\text{-}III})_2)_xC(O)H$, $-C(O)(C(R^{2\text{-}III})_2)_yC(O)H$, $-(C(R^{2\text{-}III})_2)_xC(O)R^{3\text{-}III}$, or $-C(O)(C(R^{2\text{-}III})_2)_yC(O)R^{3\text{-}III}$;

$R^{2\text{-III}}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-III}}$ is fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

$B^{1\text{-III}}$ is alkyl diradical, heteroalkyl diradical, or  ;

x represents independently for each occurrence 0, 1, 2, 3, 4, 5, 6, 7, or 8;

y represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

v represents independently for each occurrence 2, 3, or 4; and

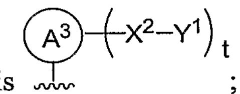
w is an integer in the range of about 5 to about 1000, inclusive; and

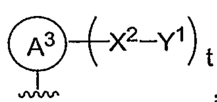
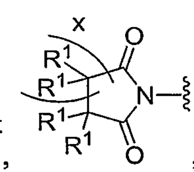
wherein compound of formlula **IV** is represented by:

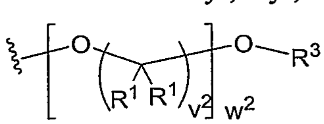
$$A^1—X^1—B—X^1—A^2$$

IV

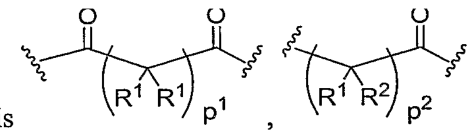
wherein

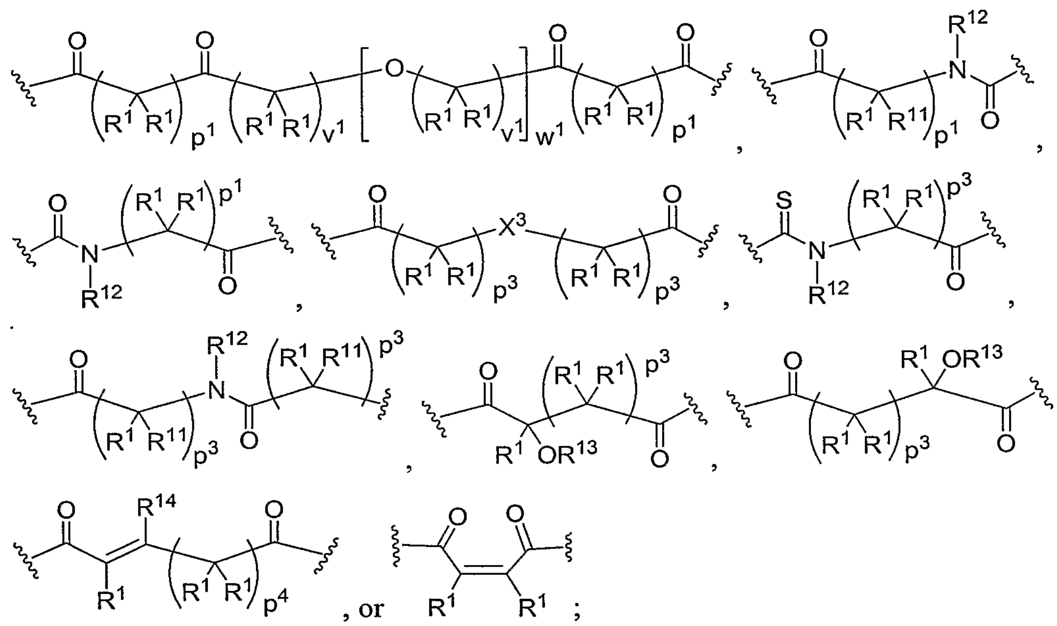
A^1 is  ;

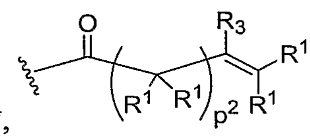
A^2 is alkyl, aryl, aralkyl,r $-Si(R^3)_3$,  ,  , or

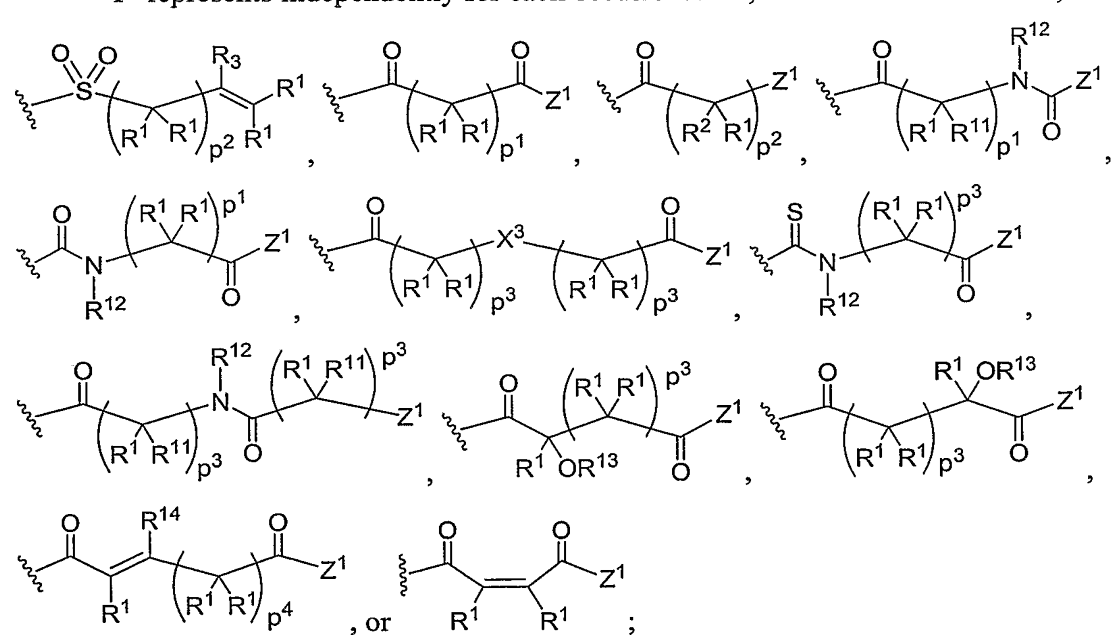
 ;

A^3 represents independently for each occurrence alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, heteroaryl, or aralkyl;

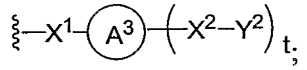
B is 



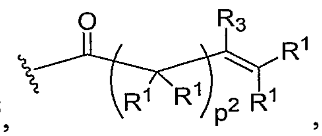
Y^1 represents independently for each occurrence R^4, 

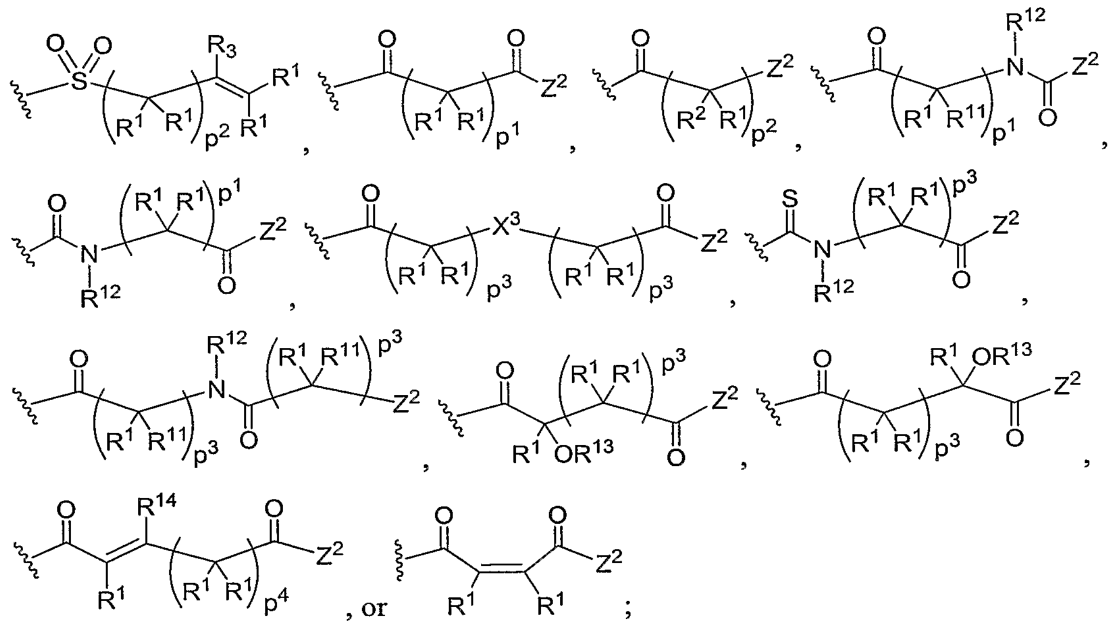


Z^1 represents independently for each occurrence $-X^1-R^4$, E, or

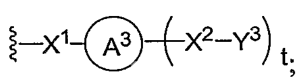


Y^2 represents independently for each occurrence R^5,

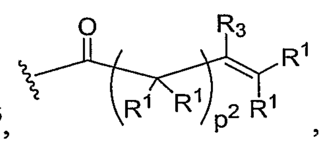


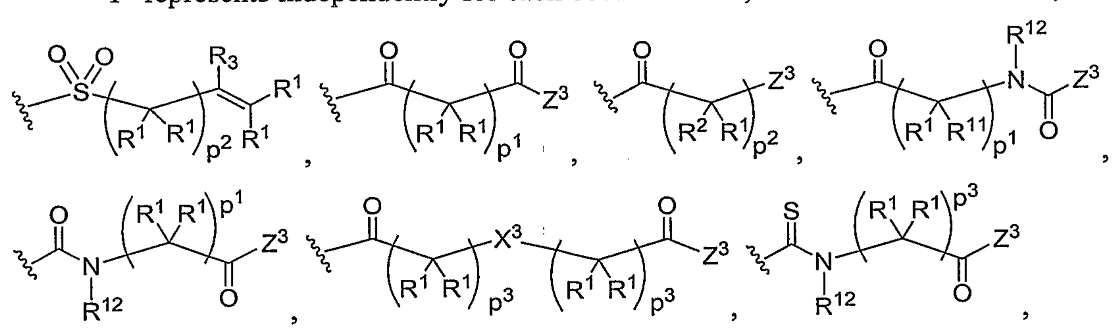


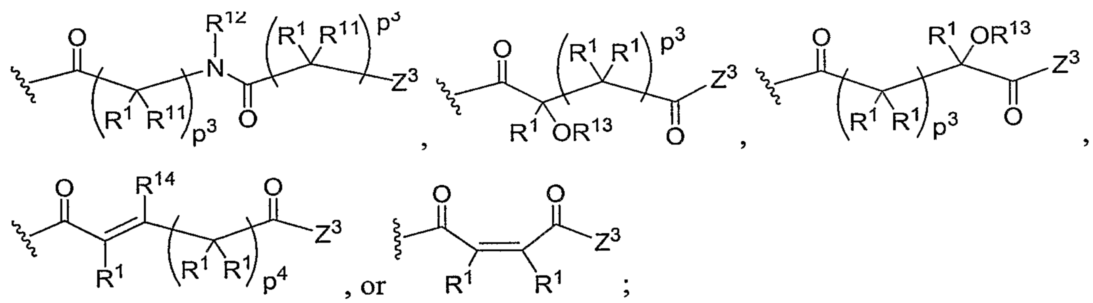
Z^2 represents independently for each occurrence $-X^1-R^5$, E, or



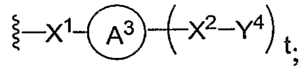
Y^3 represents independently for each occurrence R^6,



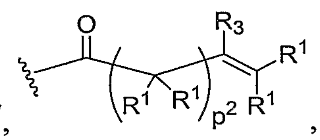


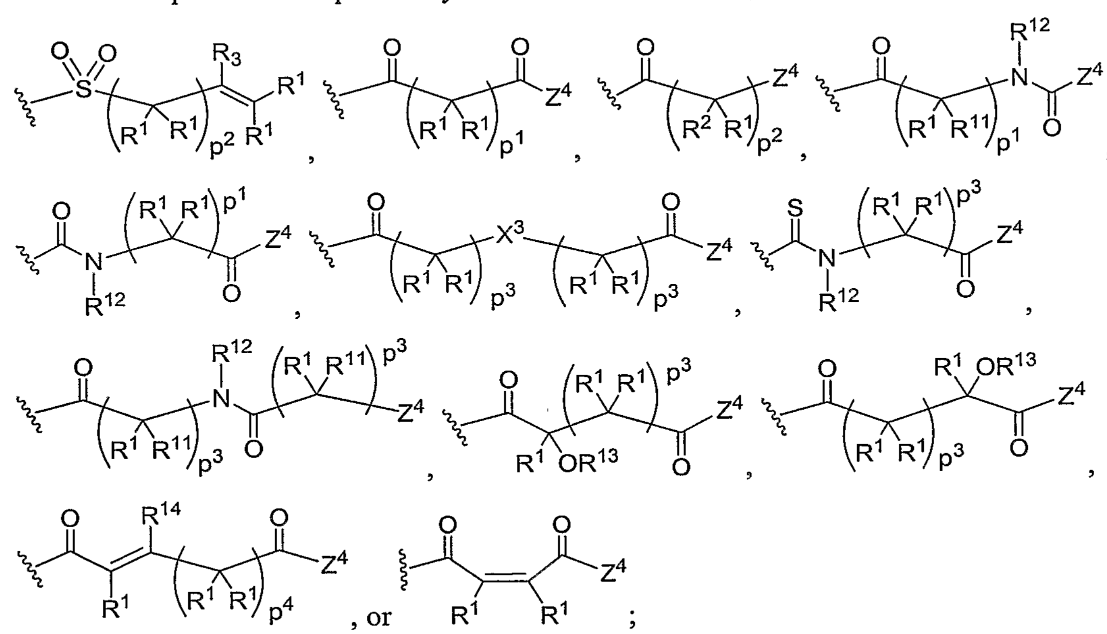


Z^3 represents independently for each occurrence $-X^1-R^6$, E, or

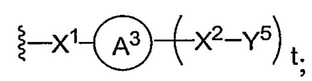


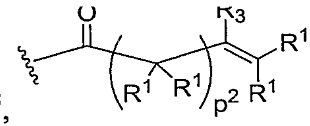
Y^4 represents independently for each occurrence R^7,

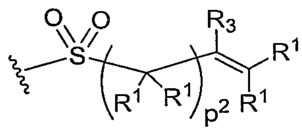
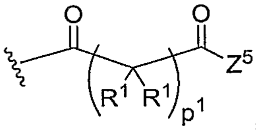
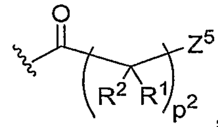
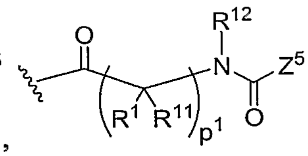


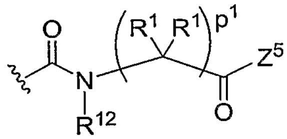
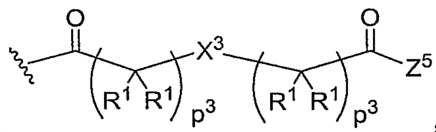
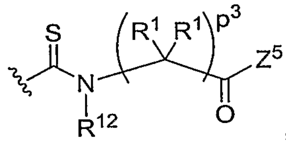


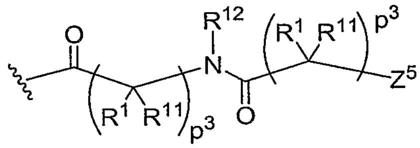
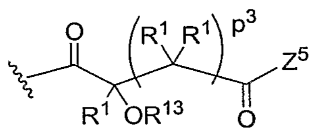
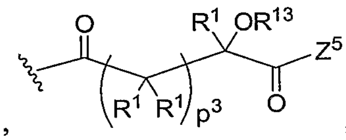
Z^4 represents independently for each occurrence $-X^1-R^7$, E, or

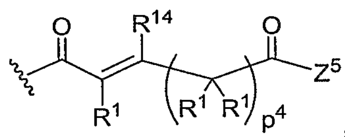
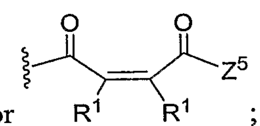


Y^5 represents independently for each occurrence R^8, ,

, , , ,

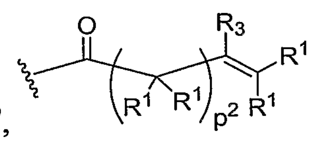
, , ,

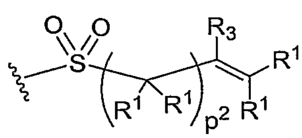
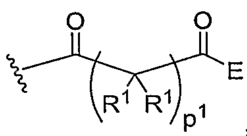
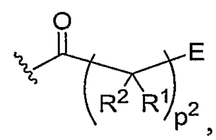
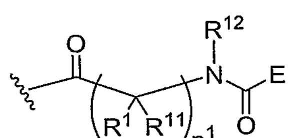
, , ,

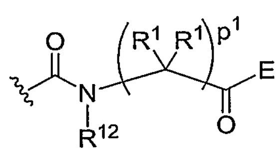
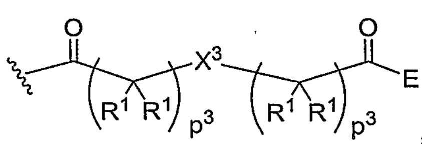
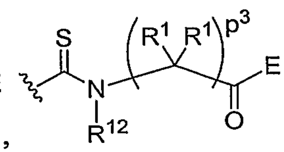
, or ;

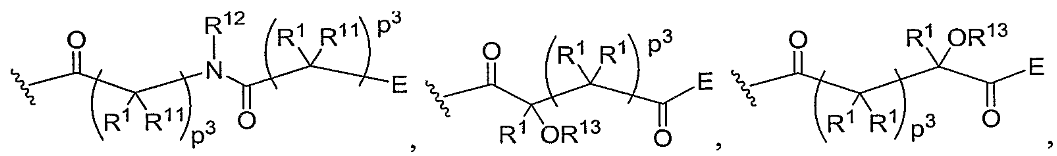
Z^5 represents independently for each occurrence $-X^1-R^8$, E, or

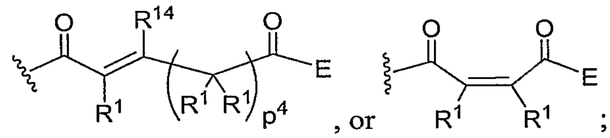
$-X^1-(A^3)-(X^2-Y^6)_t$;

Y^6 represents independently for each occurrence R^9, ,

, , , ,

, , ,





R^1 represents independently for each occurrence H, alkyl, or halogen;

R^2 represents independently for each occurrence H, alkyl, -OH, $-N(R^{10})_2$, -SH, hydroxyalkyl, or $-[C(R^1)_2]_dR^{16}$;

R^3 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^4, R^5, R^6, R^7, R^8, and R^9 are H;

R^{10} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{11} represents independently for each occurrence H, -OH, $-N(R^{10})_2$, -SH, alkyl, hydroxyalkyl, or $-[C(R^1)_2]_dR^{16}$;

R^{12} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{13} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{14} represents independently for each occurrence H, alkyl, or $-CO_2R^{10}$;

R^{15} represents independently for each occurrence H, alkyl, or $-OR^{10}$;

R^{16} represents independently for each occurrence phenyl, hydroxyphenyl, pyrrolidyl, imidazolyl, indolyl, $-N(R^{10})_2$, -SH, -S-alkyl, $-CO_2R^{10}$, $-C(O)N(R^{10})_2$, or -$C(NH_2)N(R^{10})_2$;

n represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

p^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7; or 8;

p^2 represents independently for each occurrence 0, 1, 2, 3, or 4;

p^3 represents independently for each occurrence 1, 2, or 3;

p^4 represents independently for each occurrence 0, 1, 2, or 3;

d represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

t represents independently for each occurrence 2, 3, 4, or 5 in accord with the rules of valence;

v^1 and v^2 each represent independently for each occurrence 2, 3, or 4;

w^1 and w^2 each represent independently for each occurrence an integer from about 5 to about 700, inclusive;

x is 1, 2, or 3;

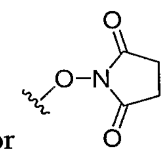
y is 0, 1, 2, 3, 4, or 5;

z^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

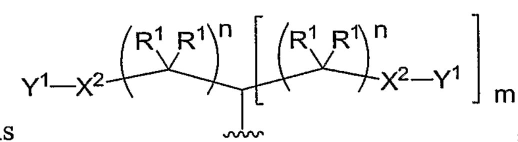
z^2 and z^3 each represent independently for each occurrence 1, 2, 3, 4, or 5;

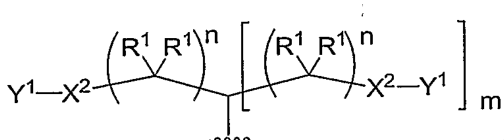
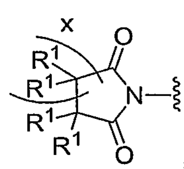
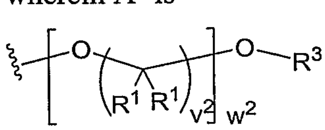
X^1 and X^2 each represent independently for each occurrence O or $-N(R^{10})-$;

X^3 represents independently for each occurrence O, $N(R^{10})$, or $C(R^{15})(CO_2R^{10})$; and

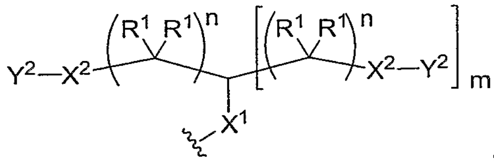
E represents independently for each occurrence H, $-[C(R^1)_2]_nC(O)H$, or .

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is ultraviolet light, visible light, a compound of formula **II**, a compound of formula **III**, or an oxidizing agent.

In certain instances, the present invention relates to the aforementioned method, wherein A^1 is , and m is 1 or 2.

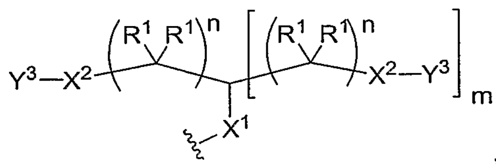
In certain instances, the present invention relates to the aforementioned method, wherein A^2 is , , , or $-Si(R^3)_3$; wherein, m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^1 represents independently for each occurrence $-X^1-R^4$ or



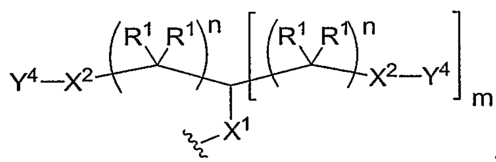
, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^2 represents independently for each occurrence $-X^1-R^5$ or



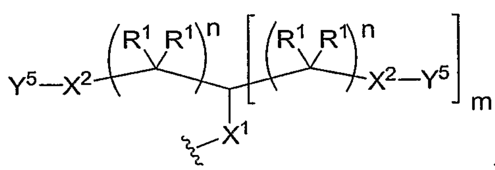
, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^3 represents independently for each occurrence $-X^1-R^6$ or



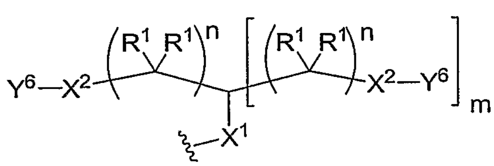
, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^4 represents independently for each occurrence $-X^1-R^7$ or



, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^5 represents independently for each occurrence $-X^1-R^8$ or



, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein X^1 is O.

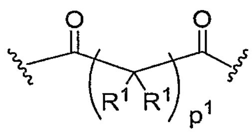
In certain instances, the present invention relates to the aforementioned method, wherein X^1 and X^2 are O.

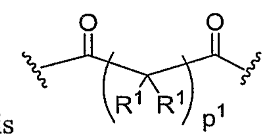
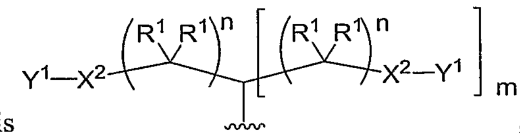
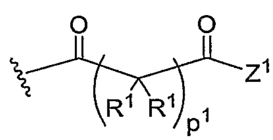
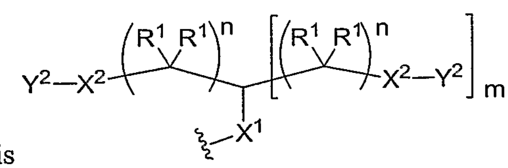
In certain instances, the present invention relates to the aforementioned method, wherein n is 1.

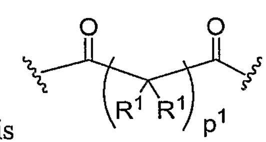
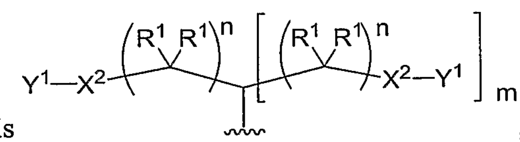
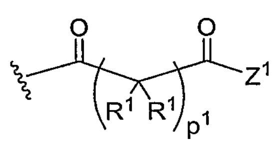
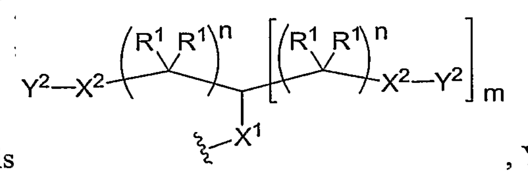
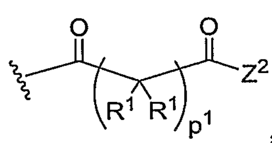
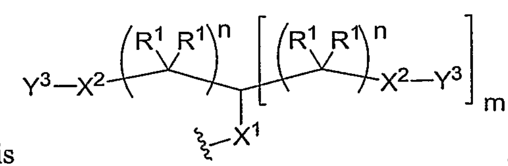
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, 3, or 4.

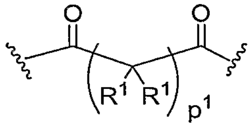
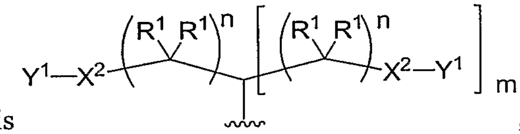
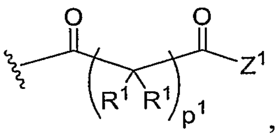
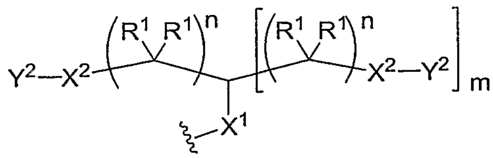
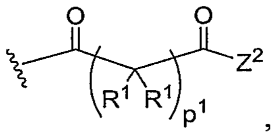
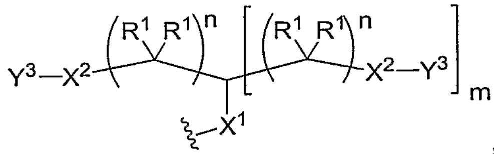
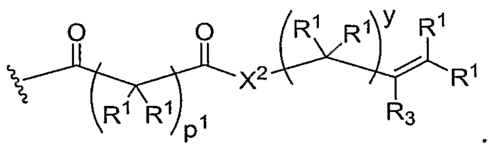
In certain instances, the present invention relates to the aforementioned method, wherein p^2 is 1.

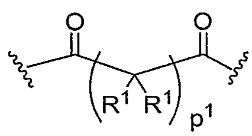
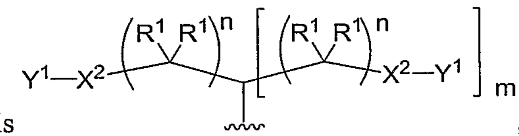
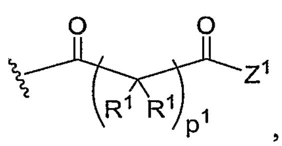
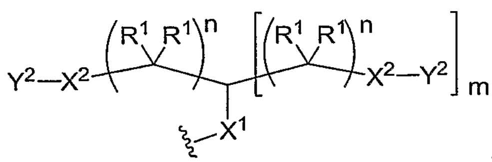
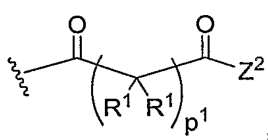
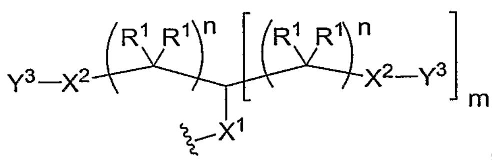
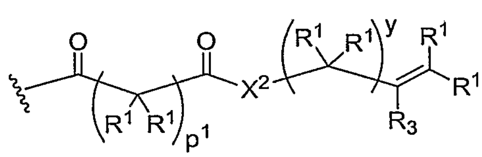
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H.

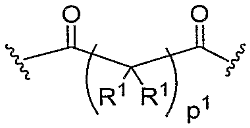
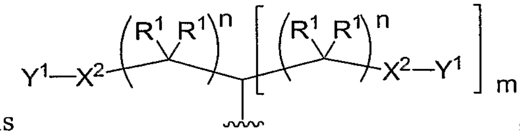
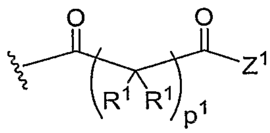
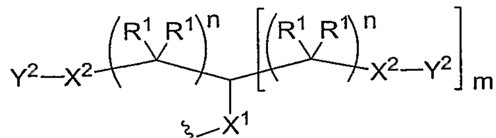
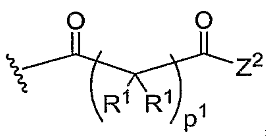
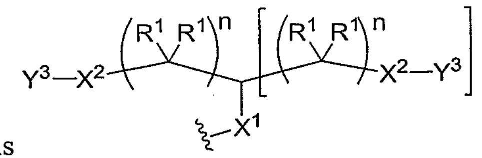
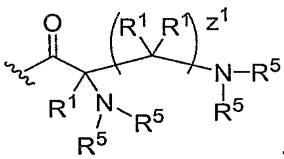
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

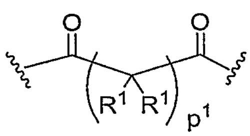
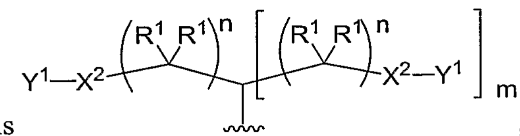
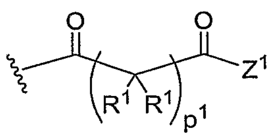
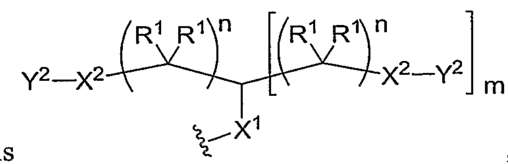
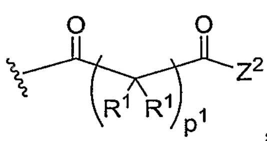
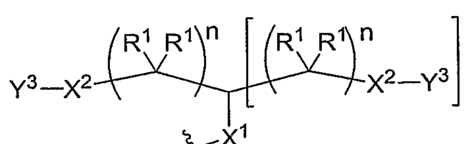
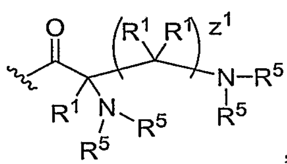
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

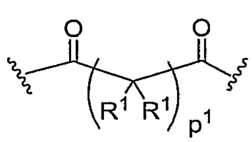
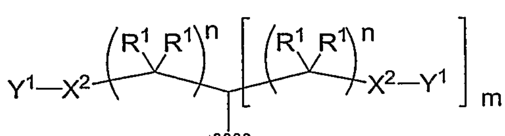
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

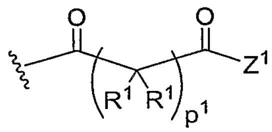
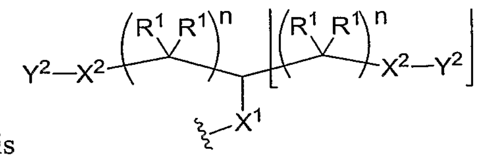
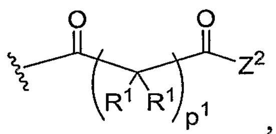
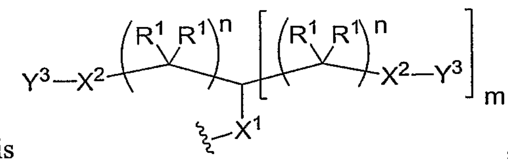
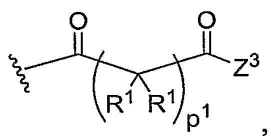
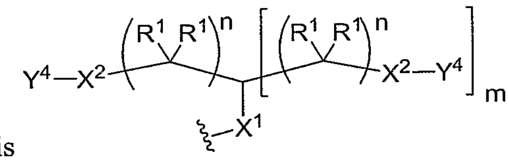
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

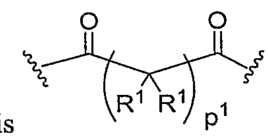
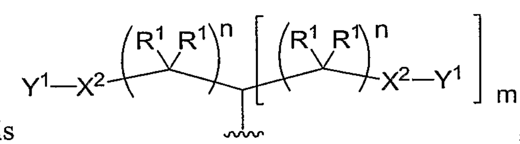
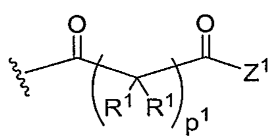
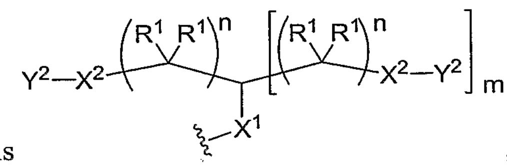
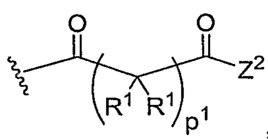
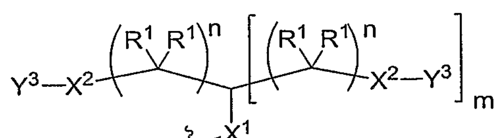
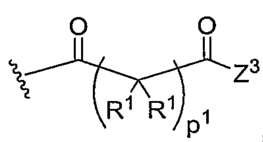
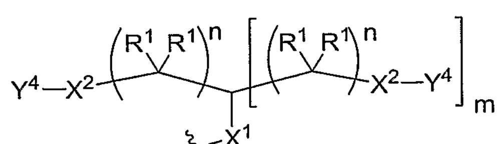
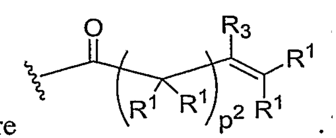
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is ultraviolet light or visible light.

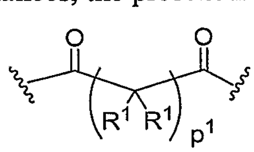
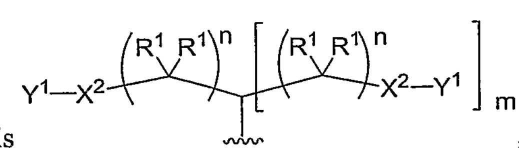
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

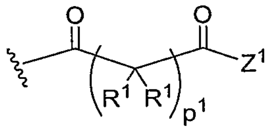
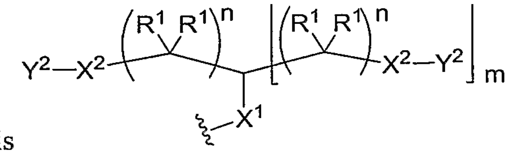
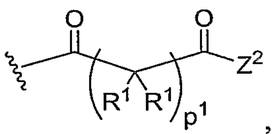
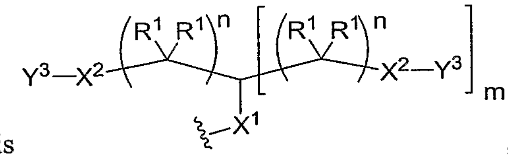
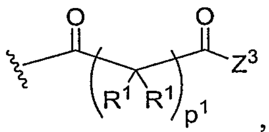
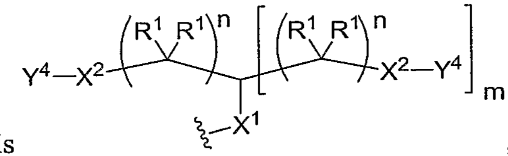
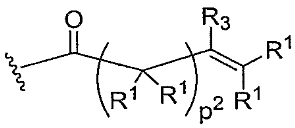
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is a compound of formula **III**.

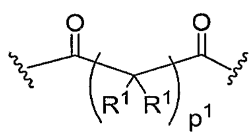
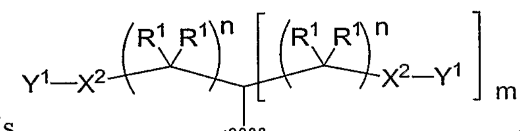
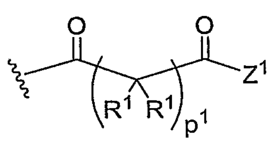
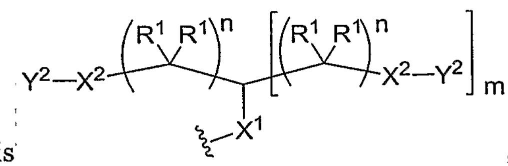
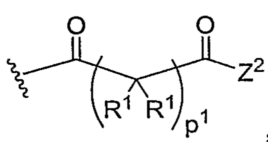
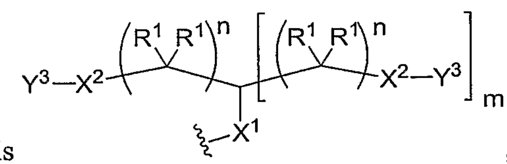
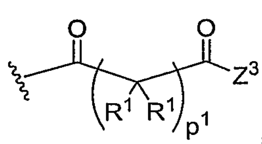
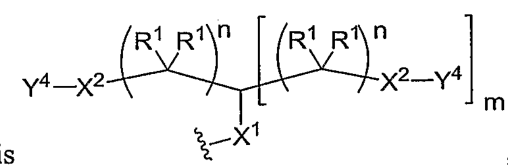
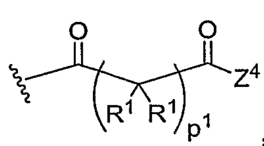
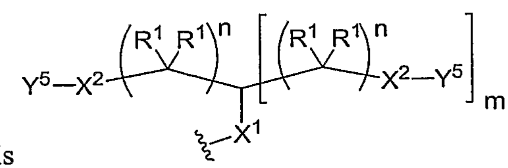
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m

is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and Z^3 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , and at least about 1/2 of the Y^4 groups are .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m

is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , at least about 1/2 of the Y^4 groups are , and said polymerization agent is ultraviolet light or visible light.

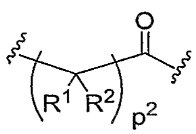
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , and Z^4 is .

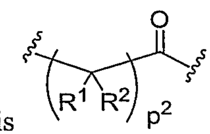
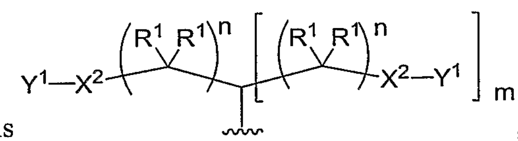
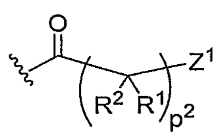
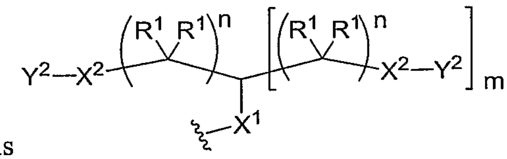
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 1, 2, 3, or 4.

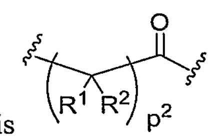
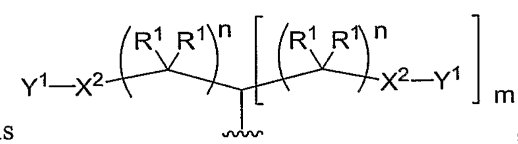
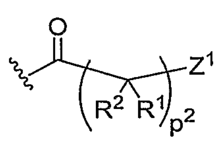
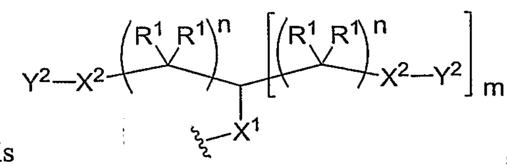
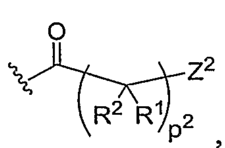
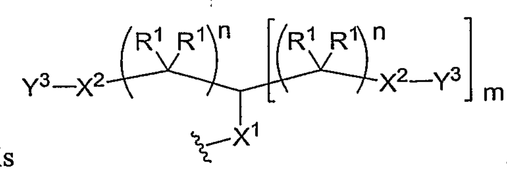
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

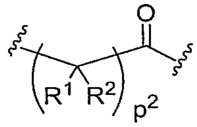
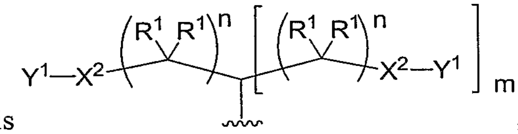
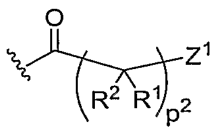
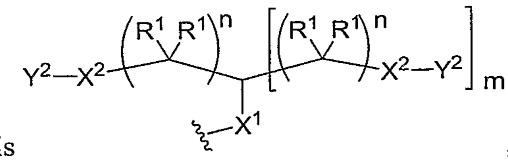
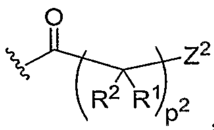
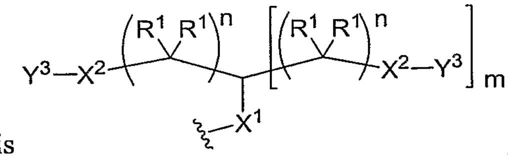
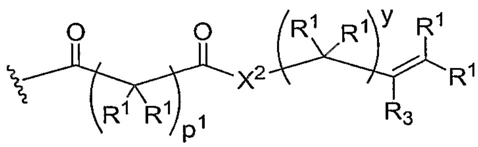
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 4.

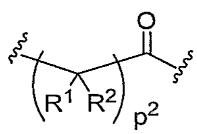
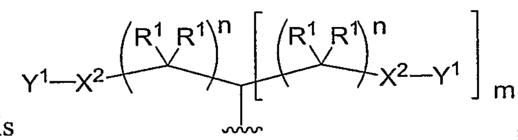
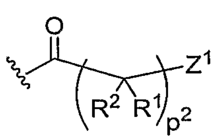
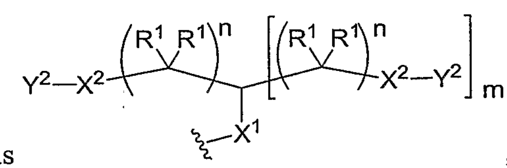
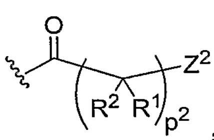
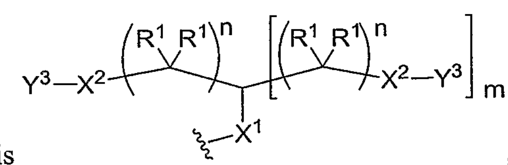
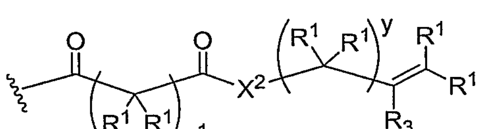
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

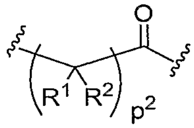
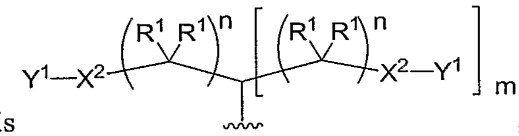
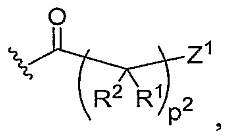
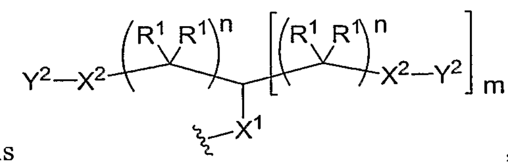
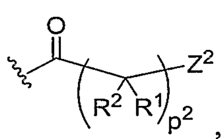
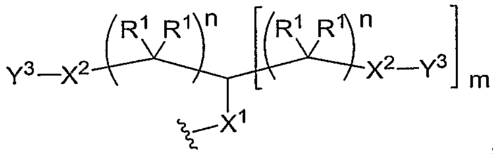
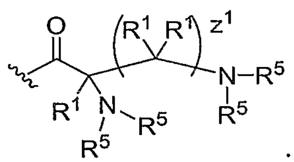
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

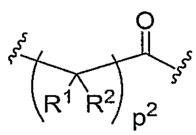
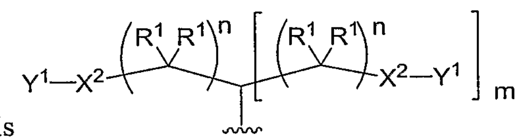
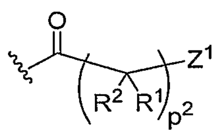
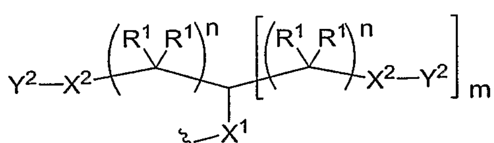
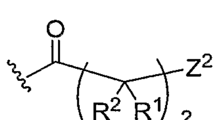
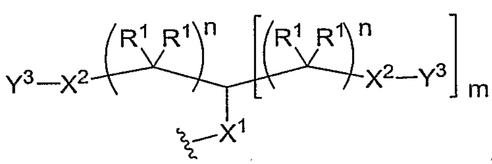
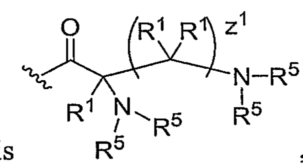
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

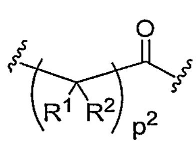
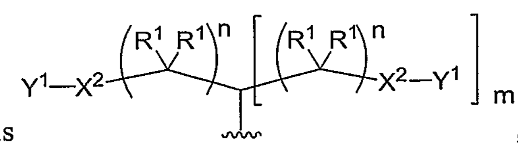
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

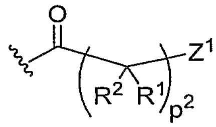
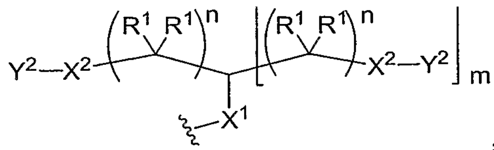
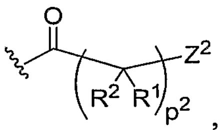
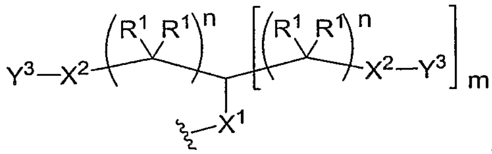
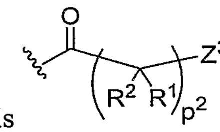
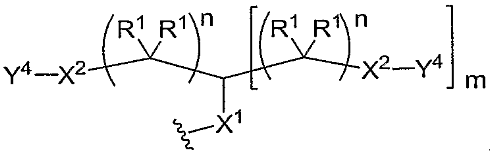
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

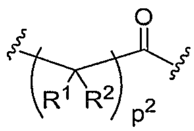
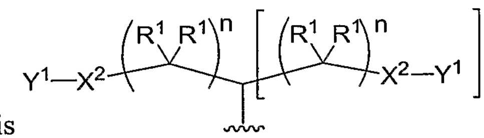
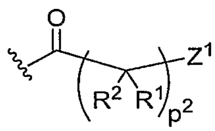
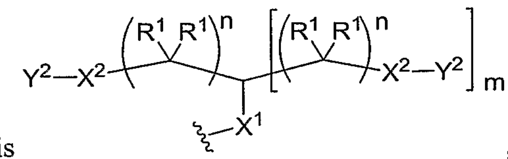
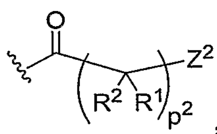
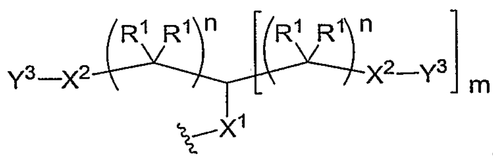
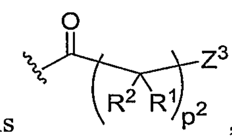
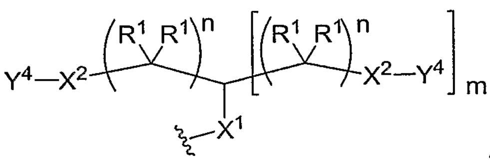
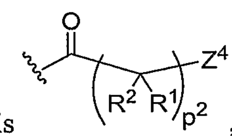
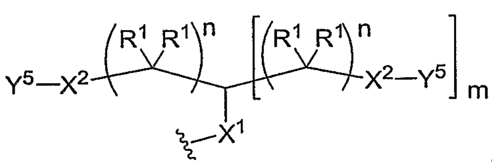
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is ultraviolet light or visible light.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , and Y^3 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and said polymerization agent is a compound of formula **III**.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1

or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and Z^3 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is  , and Z^4 is  .

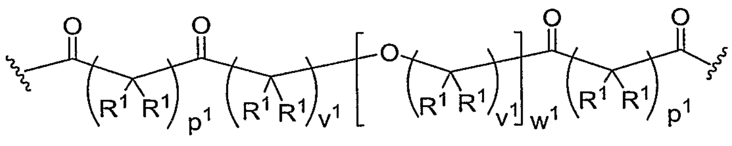
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 1, 2, 3, or 4.

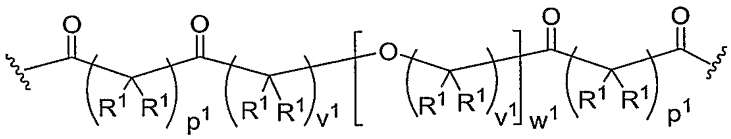
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

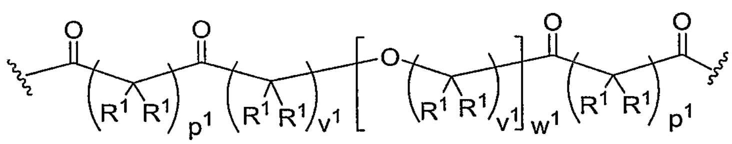
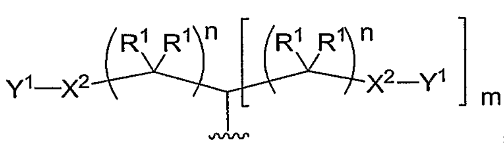
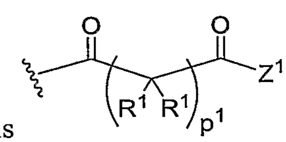
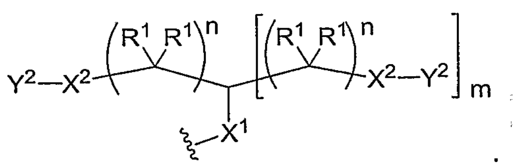
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 4.

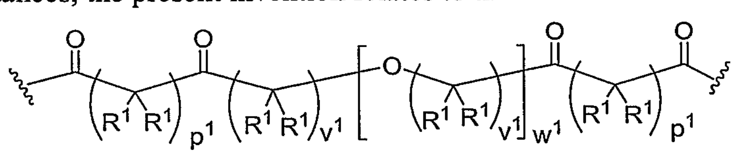
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

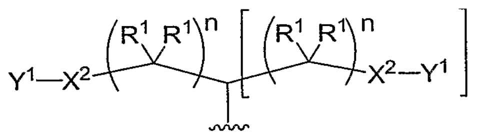
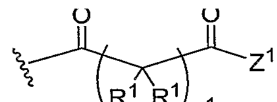
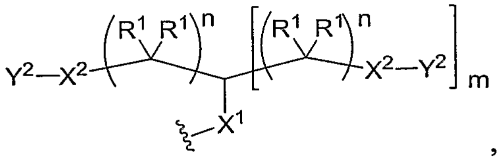
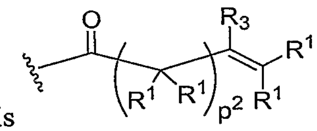
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is $(C_1\text{-}C_3)$alkyl.

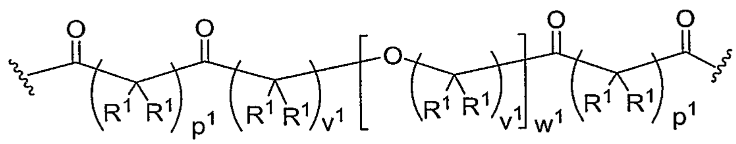
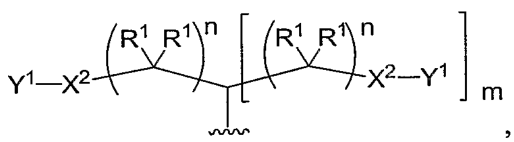
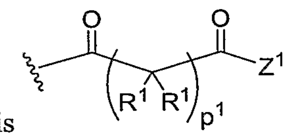
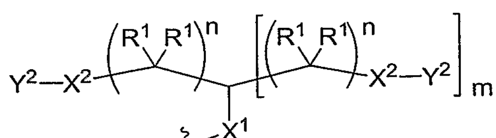
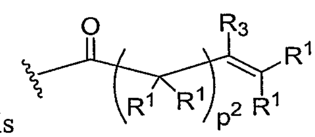
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

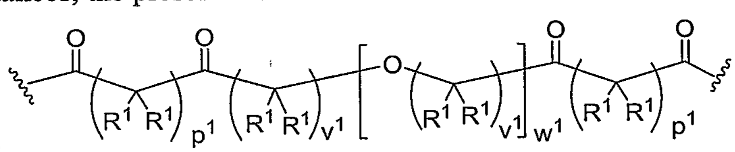
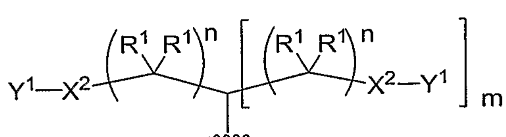
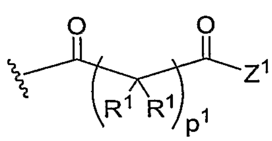
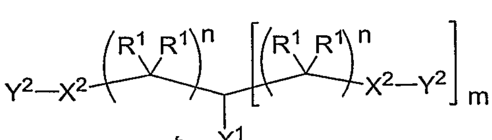
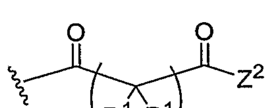
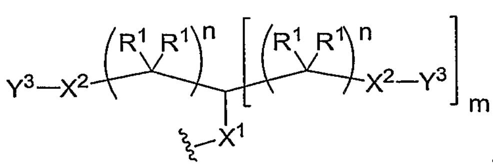
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , and v^1 is 2.

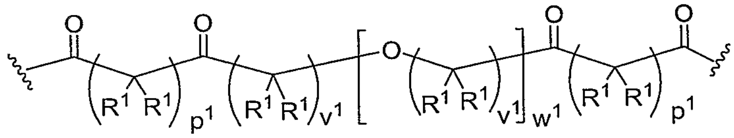
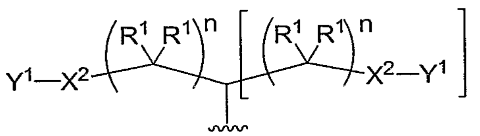
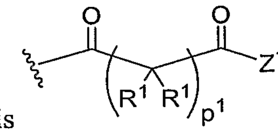
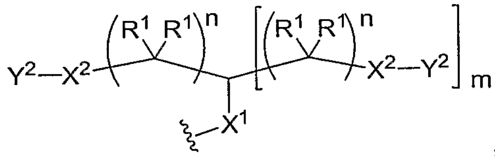
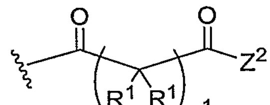
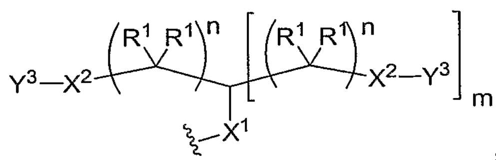
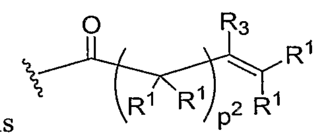
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

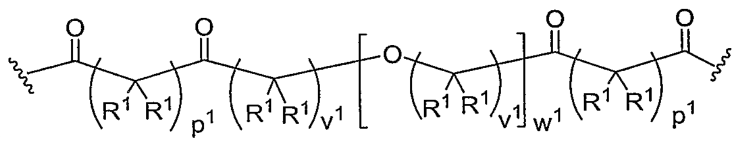
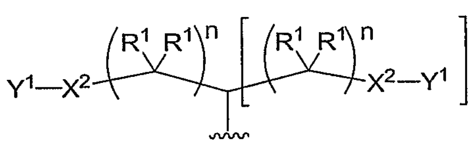
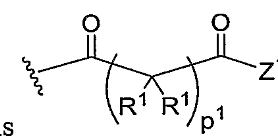
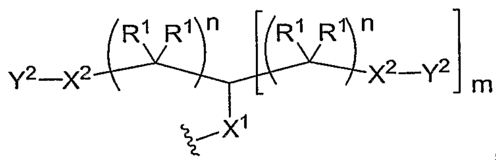
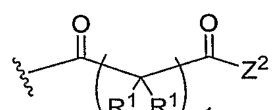
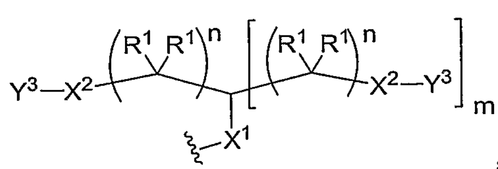
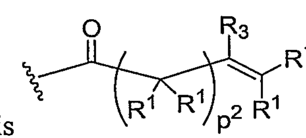
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2

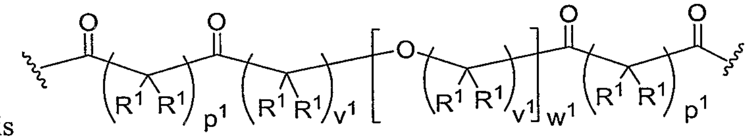
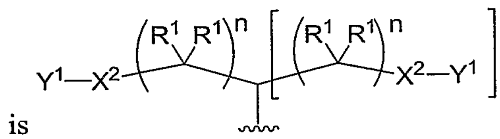
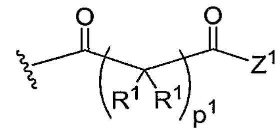
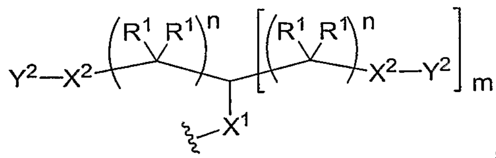
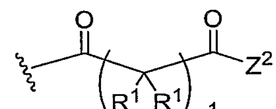
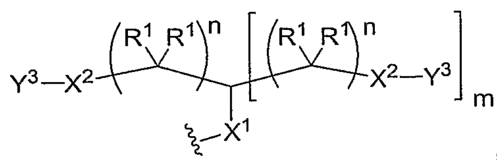
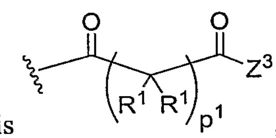
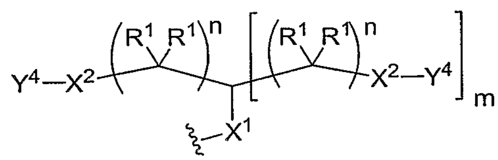
is  , m is 1 or 2, Y^1 is  , Z^1 is  , and Y^2 is  .

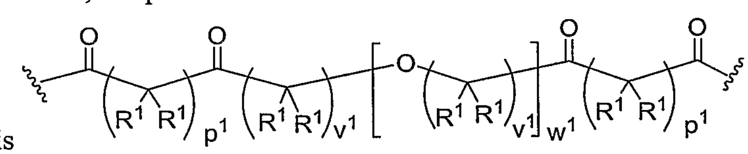
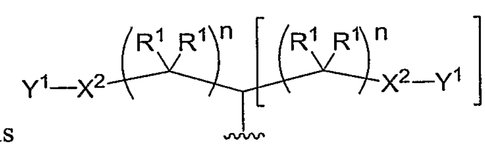
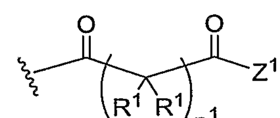
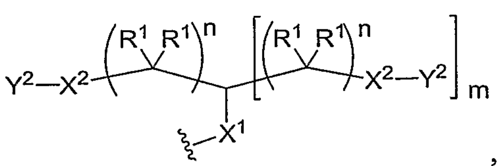
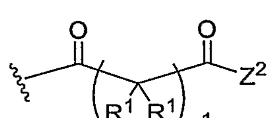
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  , Y^2 is  , and said polymerization agent is ultraviolet light or visible light.

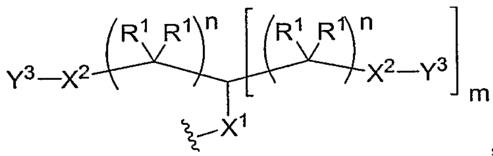
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

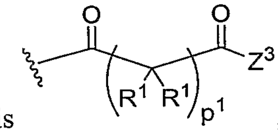
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , and Y^3 is  .

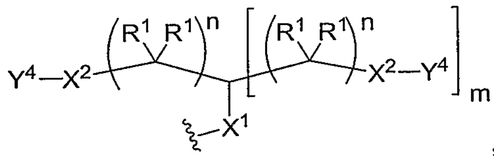
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and said polymerization agent is ultraviolet light or visible light.

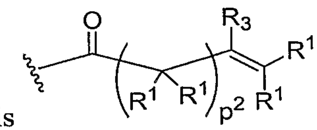
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and Z^3 is .

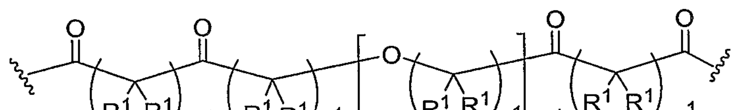
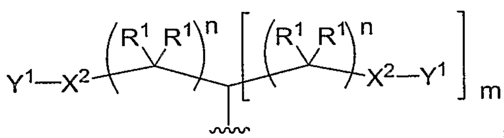
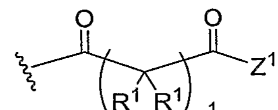
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is

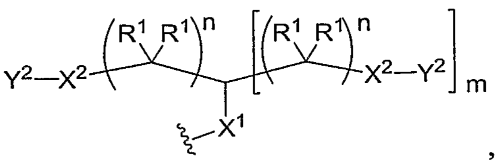


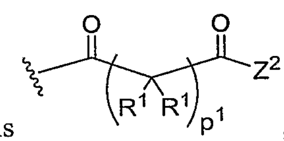
, Y^3 is  , Z^3 is

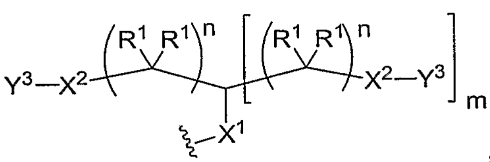


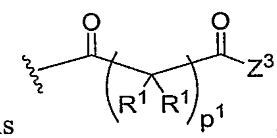
, and Y^4 is  .

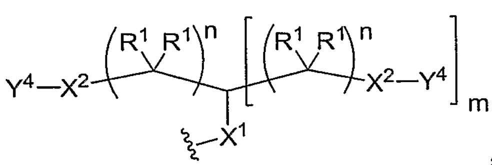
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is

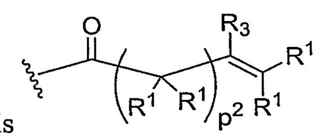


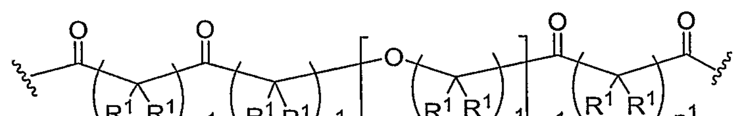
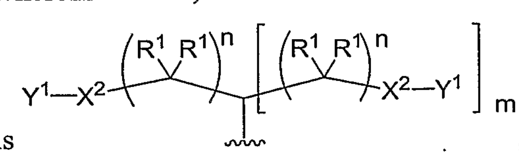
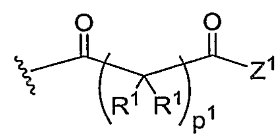
, Y^2 is  , Z^2 is

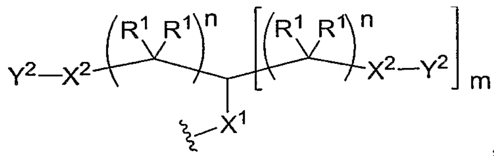
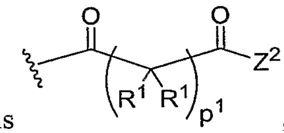


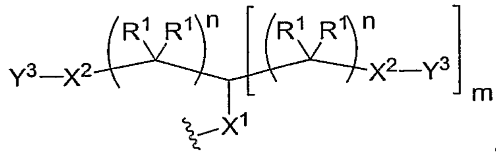
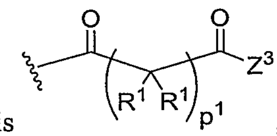
, Y^3 is  , Z^3 is

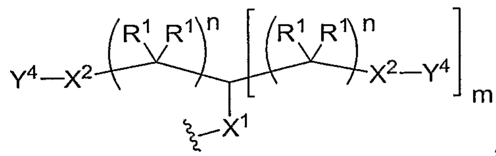
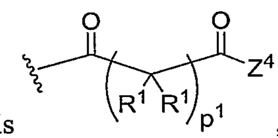


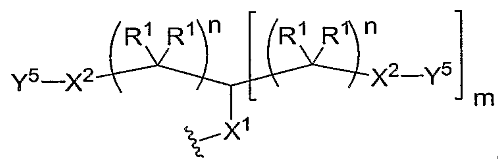
, Y^4 is  , and said polymerization agent is ultraviolet light or visible light.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is

 , Y^2 is  , Z^2 is

 , Y^3 is  , Z^3 is

 , Y^4 is  , and Z^4 is

 .

In certain instances, the present invention relates to the aforementioned method, wherin w^1 is an integer in the range of about 50 to about 250.

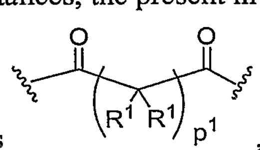
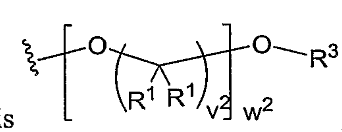
In certain instances, the present invention relates to the aforementioned method, wherein w^1 is an integer in the range of about 60 to about 90.

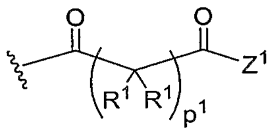
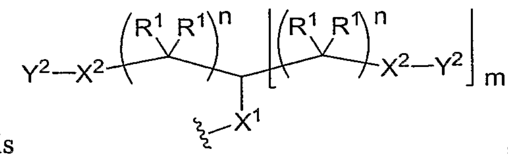
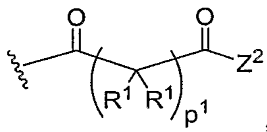
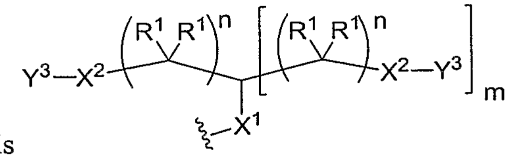
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

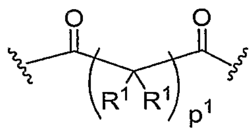
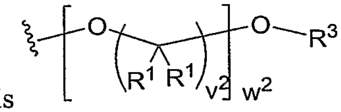
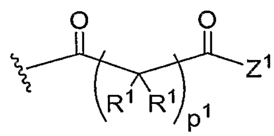
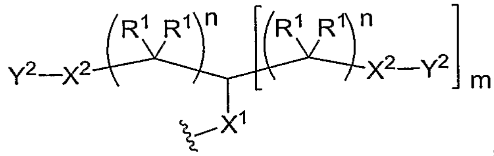
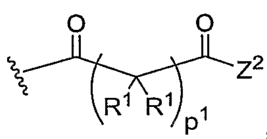
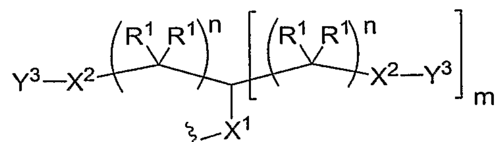
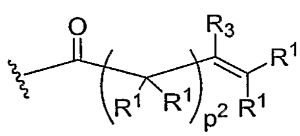
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

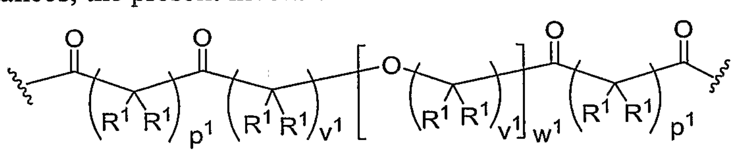
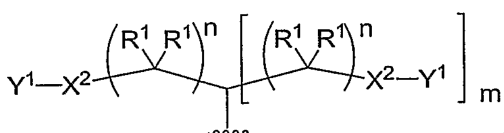
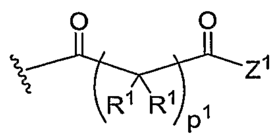
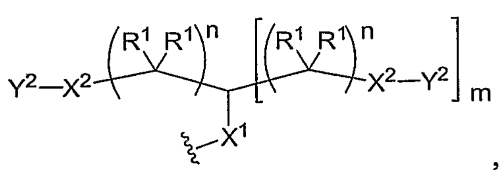
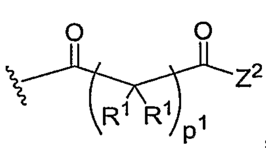
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl.

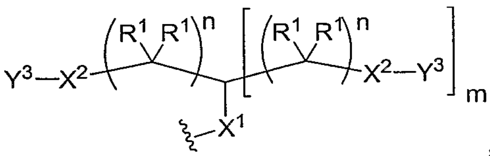
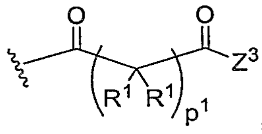
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, R^3 is $(C_1\text{-}C_5)$alkyl, and w^1 is an integer in the range of about 60 to about 90.

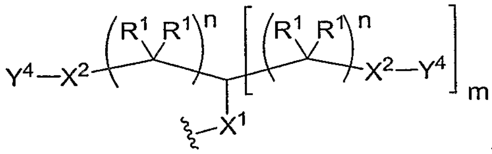
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , R^3 is alkyl, v^2 is

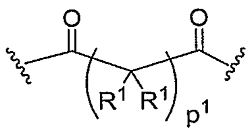
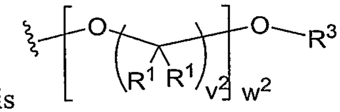
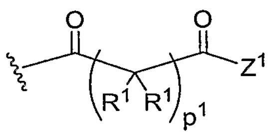
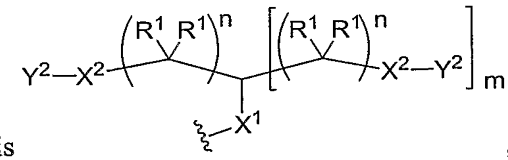
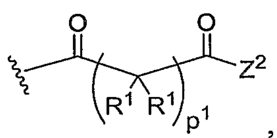
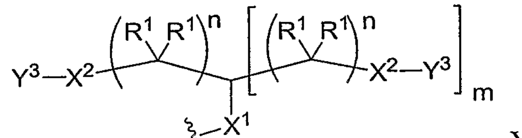
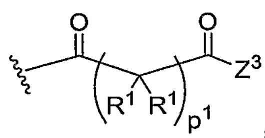
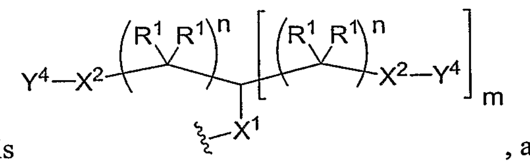
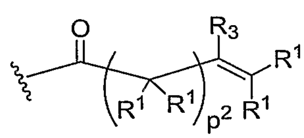
2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

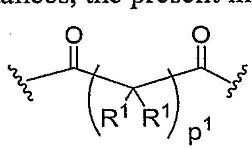
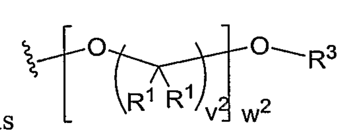
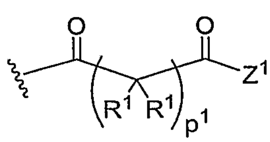
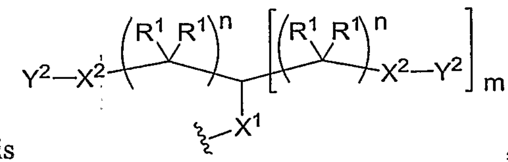
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , R^3 is alkyl, v^2 is 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , and Y^3 is  .

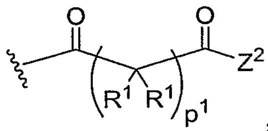
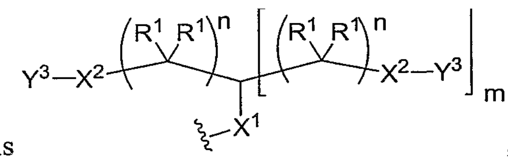
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is

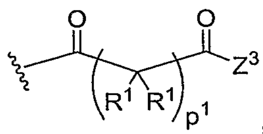
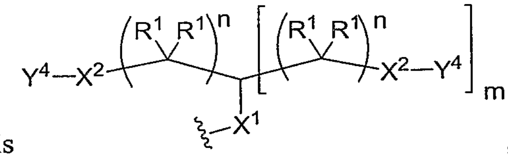
, Y^3 is , and Z^3 is

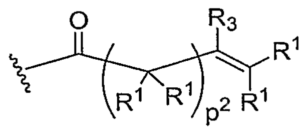
.

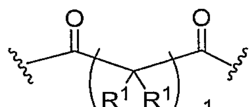
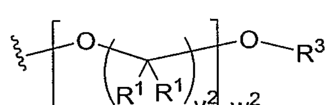
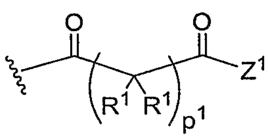
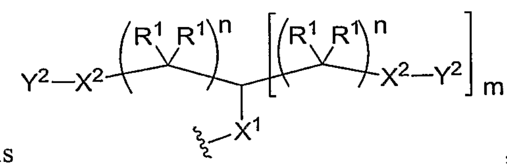
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , and Y^4 is .

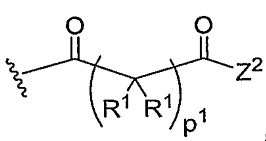
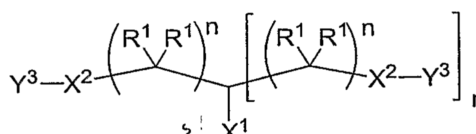
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is

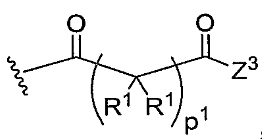
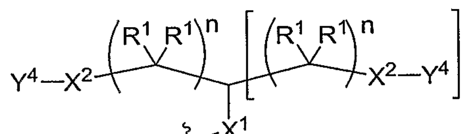
, Z^2 is , Y^3 is

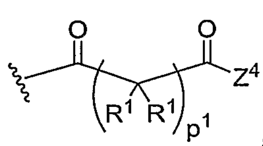
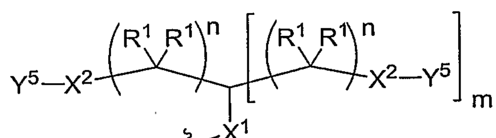
, Z^3 is , Y^4 is

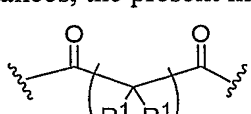
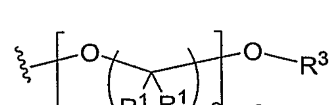
, and said polymerization agent is ultraviolet light or visible light.

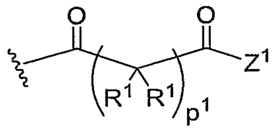
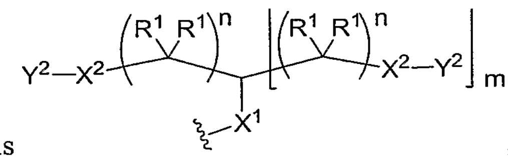
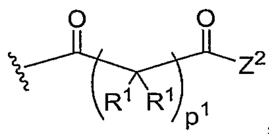
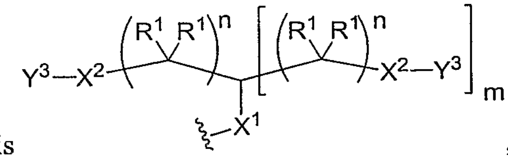
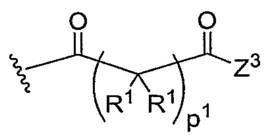
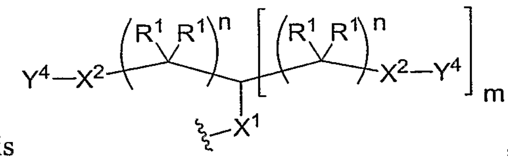
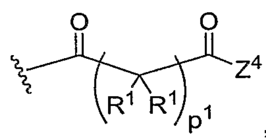
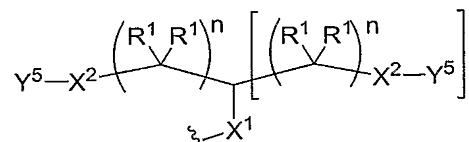
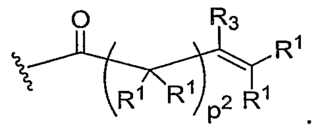
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is

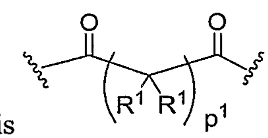
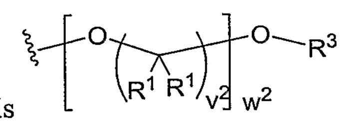
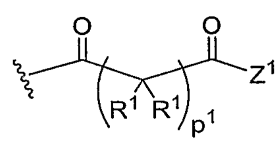
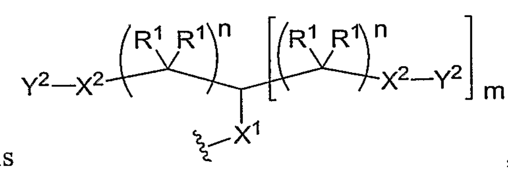
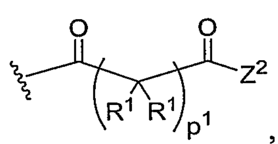
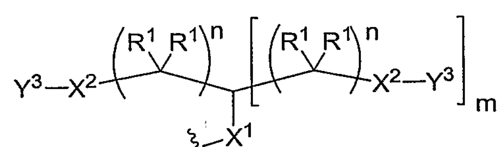
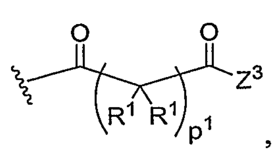
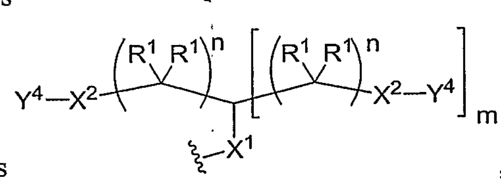
, Z^2 is , Y^3 is

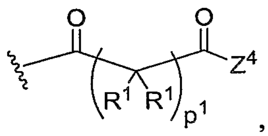
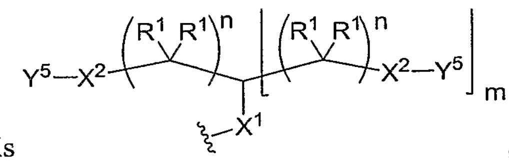
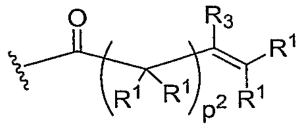
, Z^3 is , Y^4 is

, and Z^4 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is

2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , Z^4 is , and Y^5 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is

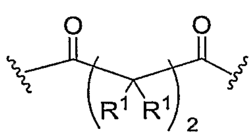
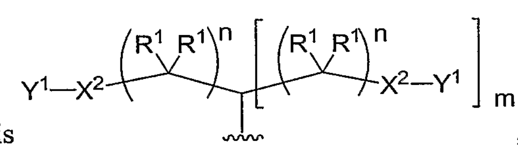
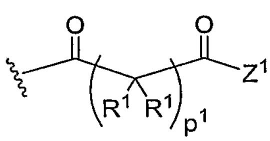
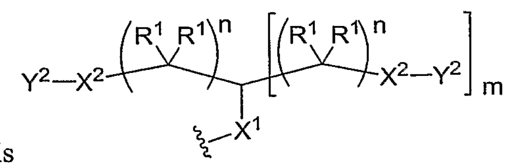
 , Z^4 is  , Y^5 is  , and said polymerization agent is ultraviolet light or visible light.

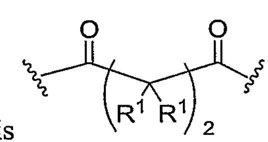
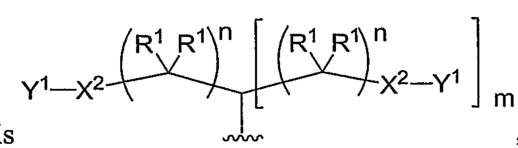
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

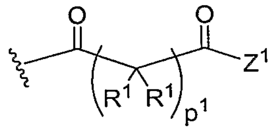
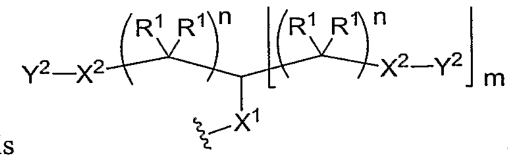
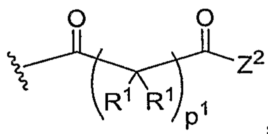
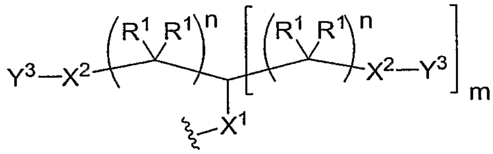
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

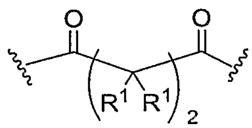
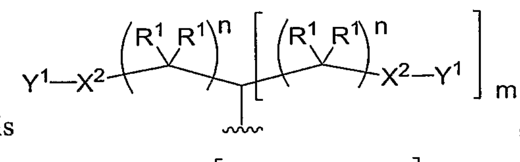
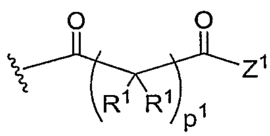
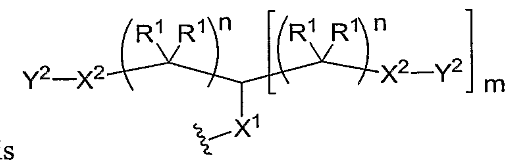
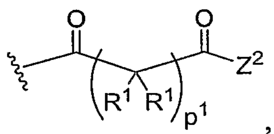
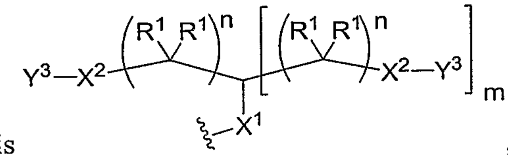
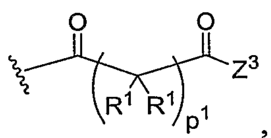
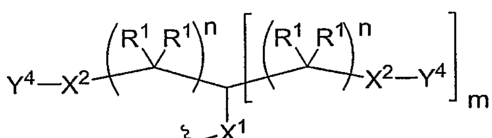
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl.

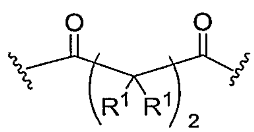
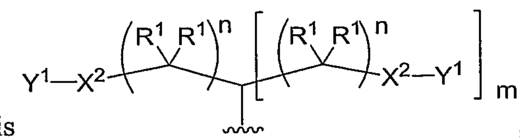
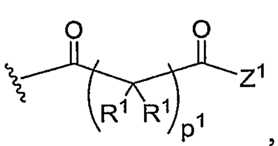
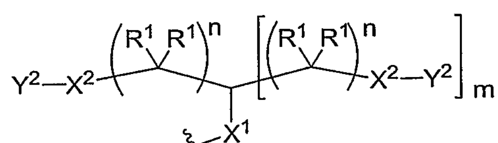
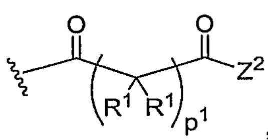
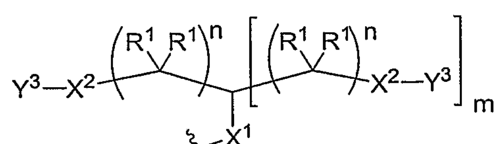
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl, and w^2 is an integer in the range of about 60 to about 90.

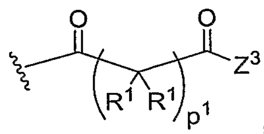
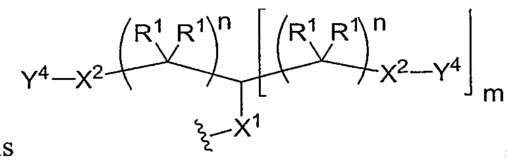
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1, or 2, Y^1 is  , and Z^1 is  .

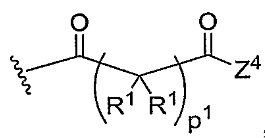
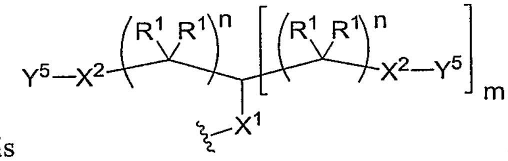
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m

is 1, or 2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1, or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and Z^3 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1, or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is

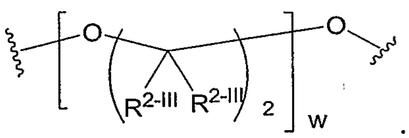
 , Z^3 is  , Y^4 is

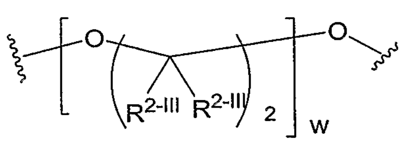
 , and Z^4 is  .

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is a compound of formula **II**.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is a compound of formula **III**.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{1\text{-}III}$ is -C(O)H, and $R^{2\text{-}III}$ is H.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{1\text{-}III}$ is -C(O)H, $R^{2\text{-}III}$ is H, and $B^{1\text{-}III}$ is  .

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{2\text{-}III}$ is -C(O)H, $R^{2\text{-}III}$ is H, $B^{1\text{-}III}$ is  , and w is an integer in the range of about 60-90.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is an oxidizing agent.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is O_2.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is ultraviolet light or visible light.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is ultraviolet light.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 400-600 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 450-550 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 488-514 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is an ophthalmic wound.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a wound to the cornea of an eye.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, corneal ulceration, retinal hole, leaking bleb, corneal transplant, trabeculectomy incision, sclerotomy incision, blepharoplasty, or skin incision.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, or corneal ulceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision or corneal laceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 25 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 15 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 10 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 5 mm long.

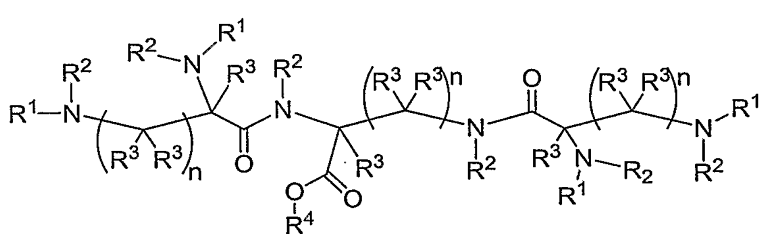
In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a method of sealing a wound of a patient, comprising the steps of:

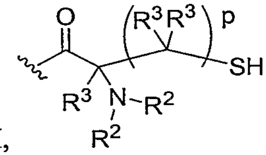
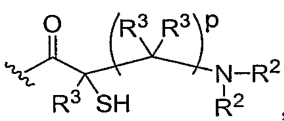
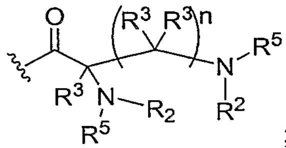
applying an effective amount of a sterilized compound of formula **V** to a wound of a patient, and exposing said sterilized compound of formula **V** to a polymerization agent sufficient to polymerize said sterilized compound of formula **V**, wherein said polymerization agent is an oxidizing agent or a compound of formula **VI**, and formula **V** is represented by:



V

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

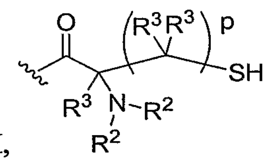
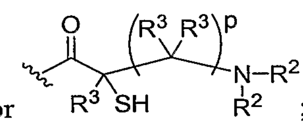
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8; and

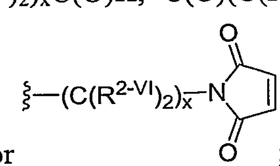
p represents independently for each occurrence 1, 2, 3, 4, or 5; and

said formula **VI** is represented by:

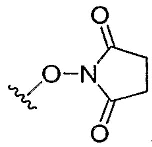
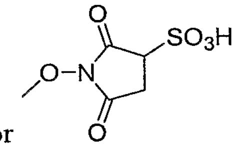
$$R^{1\text{-}VI}\!-\!B\!-\!R^{1\text{-}VI}$$

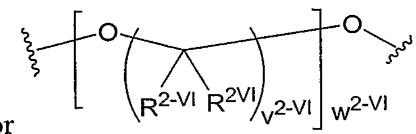
VI

wherein

$R^{1\text{-}VI}$ represents independently for each occurrence $-(C(R^{2\text{-}VI})_2)_xC(O)H$, $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)H$, $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$, $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, or ;

$R^{2\text{-}VI}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}VI}$ represents independently for each occurrence fluoroalkyl, chloroalkyl, -CH_2NO_2, , or ;

B is alkyl diradical, heteroalkyl diradical, or ;

$v^{2\text{-}VI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}VI}$ is an integer in the range of about 5 to 1000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is an oxidizing agent.

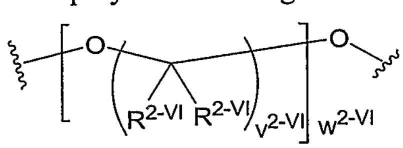
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is O_2.

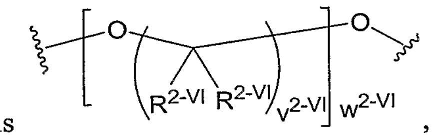
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**.

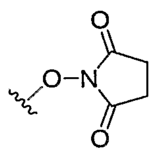
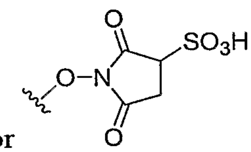
In certain instances, the present invention relates to the aforementioned method, wherein $w^{2\text{-}VI}$ is an integer in the range of about 50 to about 250.

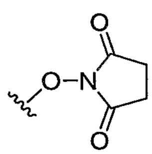
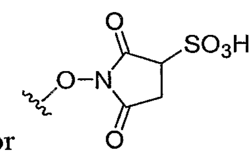
In certain instances, the present invention relates to the aforementioned method, wherein $w^{2\text{-}VI}$ is an integer in the range of about 60 to about 90.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, and $R^{2\text{-}VI}$ is H.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, $R^{2\text{-}VI}$ is H, B is , and $v^{2\text{-}VI}$ is 2.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, $R^{2\text{-}VI}$ is H, B is , $v^{2\text{-}VI}$ is 2, and $w^{2\text{-}VI}$ is an integer in the range of about 60-90.

In certain instances, the present invention relates to the aforementioned method, wherein $R^{1\text{-}VI}$ is $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$ or $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, $R^{2\text{-}VI}$ is H, and $R^{3\text{-}VI}$ is  or  .

In certain instances, the present invention relates to the aforementioned method, wherein $R^{1\text{-}VI}$ is $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$ or $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, $R^{2\text{-}VI}$ is H, $R^{3\text{-}VI}$ is  or , $v^{2\text{-}VI}$ is 2, and $w^{2\text{-}VI}$ is an integer in the range of about 15-90.

In certain instances, the present invention relates to the aforementioned method, wherein n is 3, 4, or 5.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4.

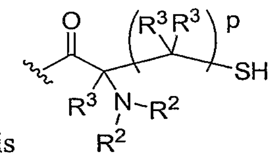
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is H.

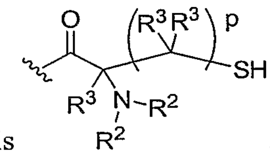
In certain instances, the present invention relates to the aforementioned method, wherein R^3 is H.

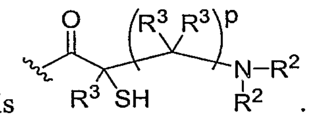
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is alkyl.

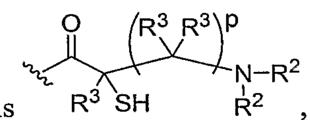
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is methyl or ethyl.

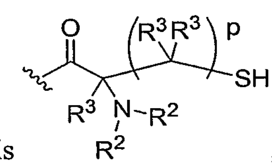
In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

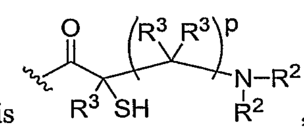
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and a Bronstead acid.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of

formula **V** and HA, wherein A is halogen or $-O_2CR^o$, and R^o is alkyl, fluoroalkyl, aryl, or aralkyl.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and an acid selected from group consisting of HCl and HBr.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and HO_2CR^6, wherein R^6 is fluoroalkyl.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and CF_3CO_2H.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is an ophthalmic wound.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a wound to the cornea of an eye.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, corneal ulceration, retinal hole, leaking bleb, corneal transplant, trabeculectomy incision, sclerotomy incision, blepharoplasty, or skin incision.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, or corneal ulceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision or corneal laceration

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 25 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 15 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 10 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 5 mm long.

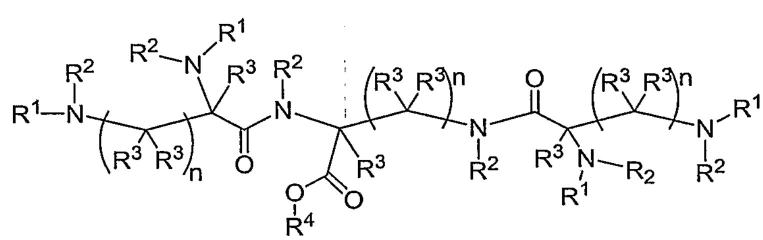
In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, said sterilized compound of formula **V** and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, said sterilized compound of formlula **V** and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a method of sealing a wound of a patient, comprising the steps of:

applying an effective amount of a dendrimeric compound of formulae **VII, VIII, IX**, or **X** to a wound of a patient and exposing said dendrimeric compound to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is an oxidizing agent or compound of formula **XI**, and wherein formula **VII** is represented by:

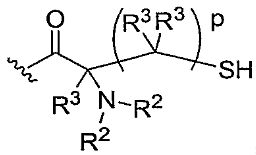
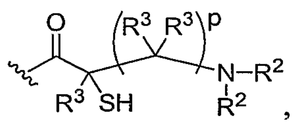
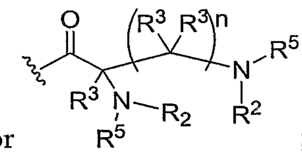


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

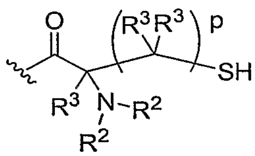
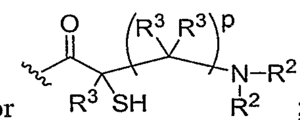

,

, or

;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

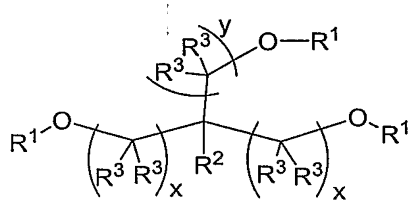
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,


, or

;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

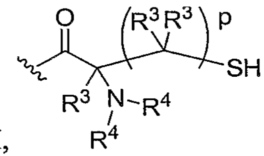
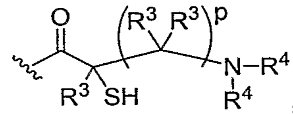
formula **VIII** is represented by:

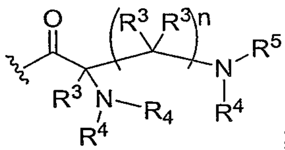


VIII

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or

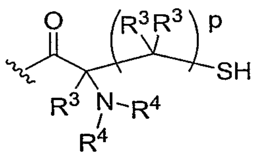
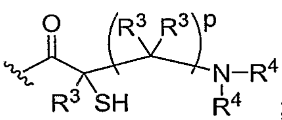
 ;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

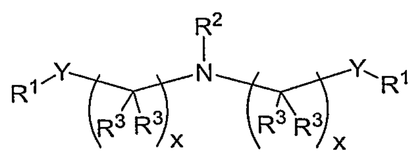
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

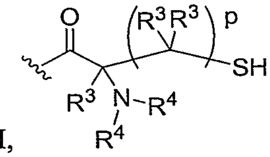
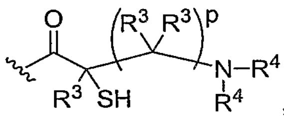
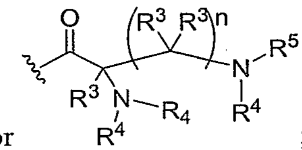
y is 0, 1, 2, 3, or 4;

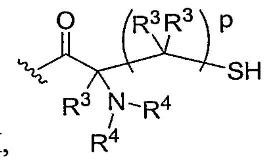
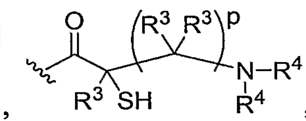
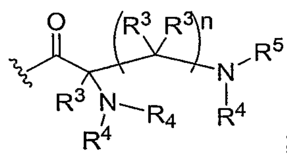
formula **IX** is represented by:



IX

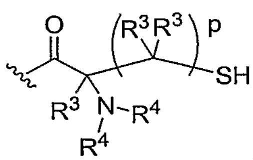
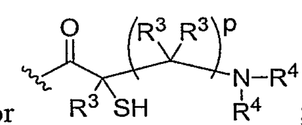
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

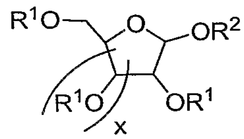
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

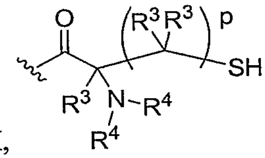
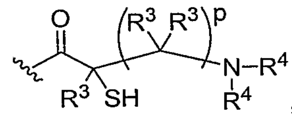
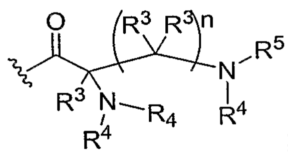
x represents independently for each occurrence 1, 2, 3, or 4;

formula **X** is represented by:



X

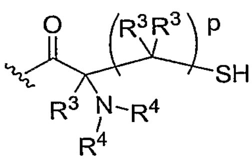
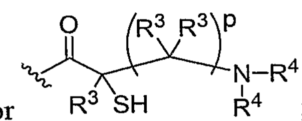
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or  ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  , or  ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2; and

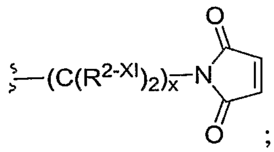
formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

XI

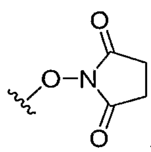
wherein

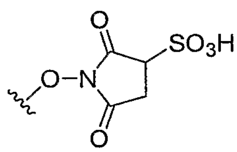
$R^{1\text{-}XI}$ represents independently for each occurrence $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yR^{4\text{-}XI}$, or


;

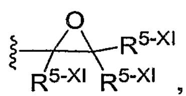
$R^{2\text{-}XI}$ represents independently for each occurrence H, alkyl, or halogen;

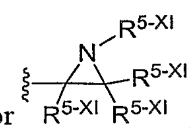
$R^{3\text{-}XI}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2,


, or


;

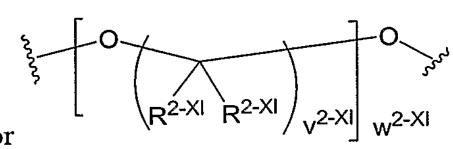
$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S,


, or


;

$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or


;

$v^{2\text{-}XI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}XI}$ is an integer in the range of about 5 to 1000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

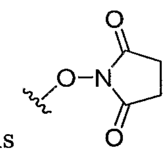
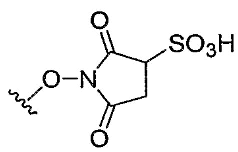
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is an oxidizing agent.

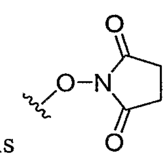
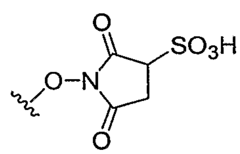
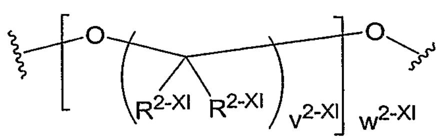
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is O_2.

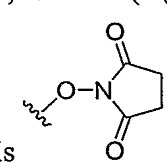
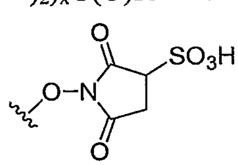
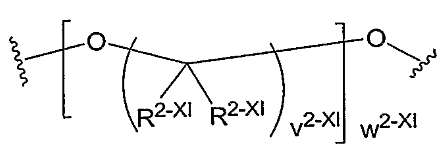
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**.

In certain instances, the present invention relates to the aforementioned method, wherein w^{2-XI} is an integer in the range of about 50 to about 250.

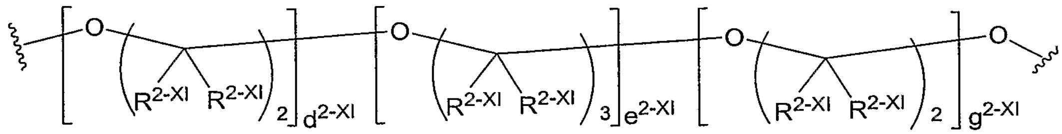
In certain instances, the present invention relates to the aforementioned method, wherein w^{2-XI} is an integer in the range of about 60 to about 90.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, R^{1-XI} is $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$ or $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, R^{2-XI} is H, and R^{3-XI} is  or  .

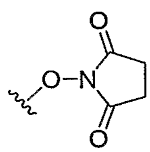
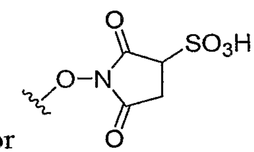
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, R^{1-XI} is $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$ or $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, R^{2-XI} is H, R^{3-XI} is  or  , B is  , and v^{2-XI} is 2.

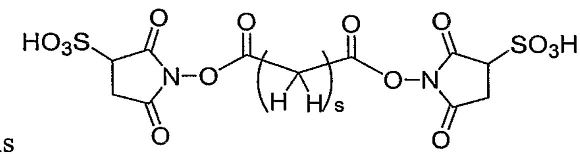
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, R^{1-XI} is $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$ or $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, R^{2-XI} is H, R^{3-XI} is  or  , B is  , v^{2-VII} is 2, and w^{2-XI} is an integer in the range of about 15-90.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, wherein B is



, and $d^{2\text{-XI}}$, $e^{2\text{-XI}}$, and $g^{2\text{-XI}}$ represent independently an integer greater than zero, provided that the sum of $d^{2\text{-XI}}$, $e^{2\text{-XI}}$, and $g^{2\text{-XI}}$ is an integer in the range of about 5 to 1000, inclusive.

In certain instances, the present invention relates to the aforementioned method, wherein, $R^{1\text{-XI}}$ is $-(C(R^{2\text{-XI}})_2)_xC(O)R^{3\text{-XI}}$ or $-C(O)(C(R^{2\text{-XI}})_2)_yC(O)R^{3\text{-XI}}$, $R^{2\text{-XI}}$ is H, and $R^{3\text{-XI}}$ is  or 

In certain instances, the present invention relates to the aforementioned method, wherein, formula **XI** is  , and s is an integer in the range of about 1-20, inclusive.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VII**.

In certain instances, the present invention relates to the aforementioned method, wherein n is 3, 4, or 5.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4.

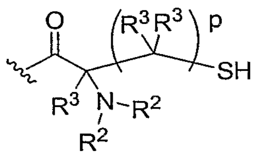
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is H.

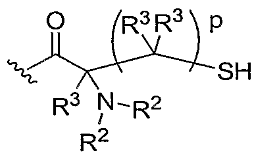
In certain instances, the present invention relates to the aforementioned method, wherein R^3 is H.

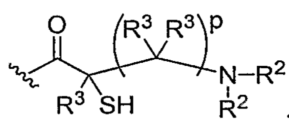
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is alkyl.

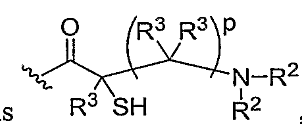
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is methyl or ethyl.

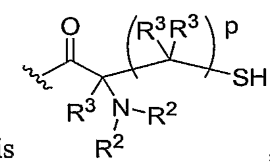
In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

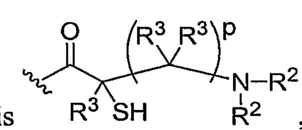
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**, x and y are 1, R^2 is -CH_2OR^1, and R^3 is H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**, x is 1, y is 0, and R^2 and R^3 are H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is O, R^2 is -$CH_2CH_2OR^1$, and R^3 is H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is NR^4, and R^2 and R^3 are H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **X**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **X**, R^2 is methyl, and x is 2.

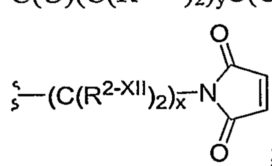
In certain instances, the present invention relates to the aforementioned method, further comprising the step of exposing said dendrimeric compound to a compound of formula **XII**, wherein formula **XII** is represented by:

$$R^{1\text{-}XII}\text{—}B^{XII}\text{—}R^{1\text{-}XII}$$

XII

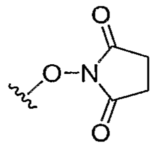
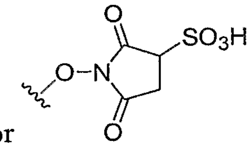
wherein

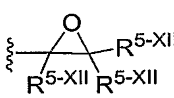
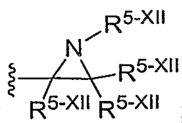
$R^{1\text{-}XII}$ represents independently for each occurrence -$(C(R^{2\text{-}XII})_2)_xC(O)R^{3\text{-}XII}$, -$C(O)(C(R^{2\text{-}XII})_2)_yC(O)R^{3\text{-}XII}$, -$(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XII}$, -$C(O)(C(R^{2\text{-}XII})_2)_yR^{4\text{-}XII}$, or



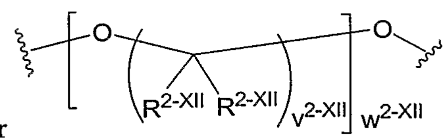
;

$R^{2\text{-}XII}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}XII}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2,  , or  ;

$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S,  , or  ;

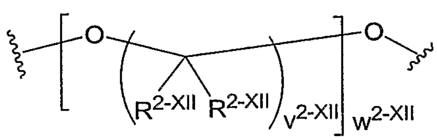
$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

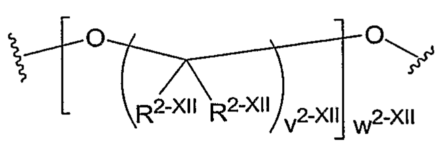
B^{XII} is alkyl diradical, heteroalkyl diradical, or  ;

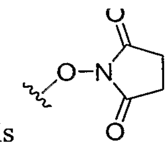
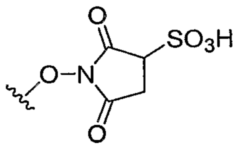
$v^{2\text{-}XII}$ represents independently for each occurrence 2, 3, or 4;

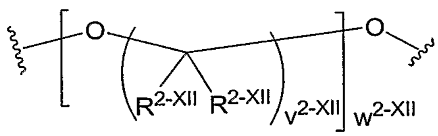
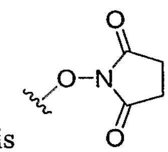
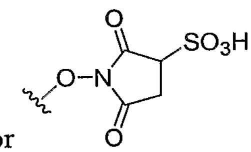
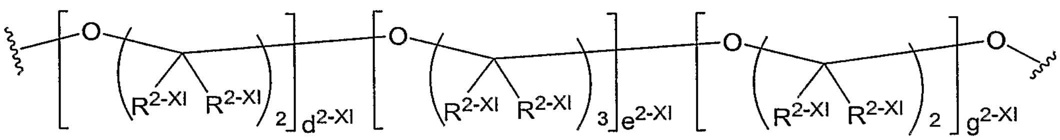
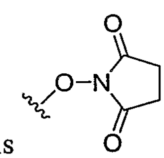
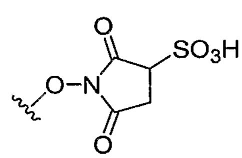
$w^{2\text{-}XII}$ is an integer in the range of about 5 to 1000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is  , and $v^{2\text{-}XII}$ is 2.

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is  , $v^{2\text{-}XII}$ is 2, $R^{1\text{-}XII}$ is -$(C(R^{2\text{-}XII})_2)_xC(O)R^{3\text{-}}$

^{XII} or -C(O)(C($R^{2\text{-}XII}$)$_2$)$_y$C(O)$R^{3\text{-}XII}$, $R^{2\text{-}XII}$ is H, and $R^{3\text{-}XII}$ is  or  .

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is  , $v^{2\text{-}XII}$ is 2, $R^{1\text{-}XII}$ is -(C($R^{2\text{-}XII}$)$_2$)$_x$C(O)$R^{3\text{-}XII}$ or -C(O)(C($R^{2\text{-}XII}$)$_2$)$_y$C(O)$R^{3\text{-}XII}$, $R^{2\text{-}XII}$ is H, $R^{3\text{-}XII}$ is  or  , said polymerization agent is a compound of formula **XI**, B is  , $R^{1\text{-}XI}$ is -(C($R^{2\text{-}XI}$)$_2$)$_x$C(O)$R^{3\text{-}XI}$ or -C(O)(C($R^{2\text{-}XI}$)$_2$)$_y$C(O)$R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or  , and $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ represent independently an integer greater than zero, provided that the sum of $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ is an integer in the range of about 5 to 500, inclusive.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is an ophthalmic wound.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a wound to the cornea of an eye.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, corneal ulceration, retinal hole, leaking bleb, corneal transplant, trabeculectomy incision, sclerotomy incision, blepharoplasty, or skin incision.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, or corneal ulceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision or corneal laceration

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 25 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 15 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 10 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 5 mm long.

In certain embodiments, the present invention relates to the aforemention method, further comprising the step of sterilizing said dendrimeric compound.

In certain embodiments, the present invention relates to the aforemention method, further comprising the step of sterilizing said dendrimeric compound and said polymerization agent, wherein said polymerization agent is a compound of formula **XI**.

In certain embodiments, the present invention relates to the aforemention method, wherein said sterilizing is performed by treatment with ethylene oxide, hydrogen peroxide, heat, gamma irradiation, electron beam irradiation, microwave irradiation, or visible light irradiation.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

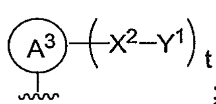
Another aspect of the present invention relates to a method of sealing a wound of a patient, comprising the steps of:

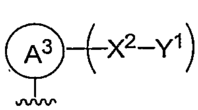
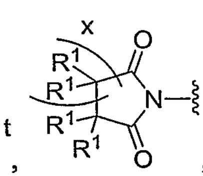
exposing a sterilized dendrimeric compound of formula **I** to a polymerization agent to form an adhesive composition, and applying said adhesive composition to a wound of a patient, wherein said polymerization agent is ultraviolet light, visible light, a compound of formula **II**, a compound of formula **III**, a compound of formula **IV**, or an oxidizing agent, and formula **I** is represented by:

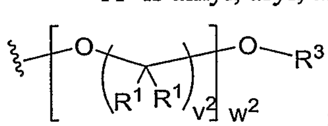
$$A^1—X^1—B—X^1—A^2$$

I

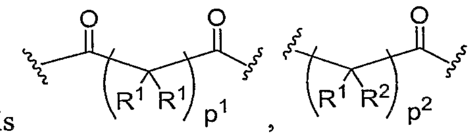
wherein

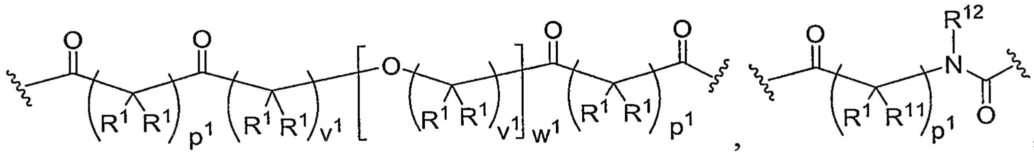
A^1 is  ;

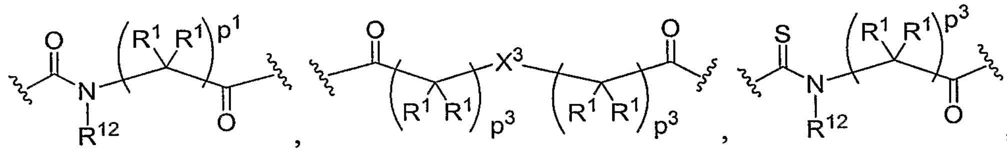
A^2 is alkyl, aryl, aralkyl, -Si(R^3)$_3$,  ,  , or

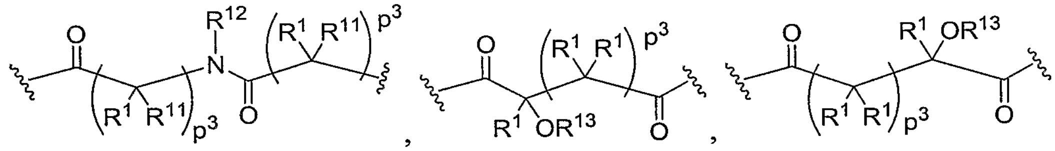
 ;

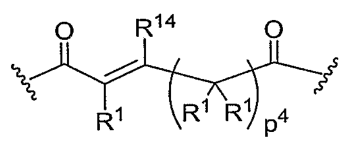
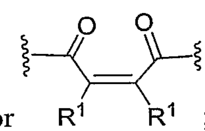
A^3 represents independently for each occurrence alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, heteroaryl, or aralkyl;

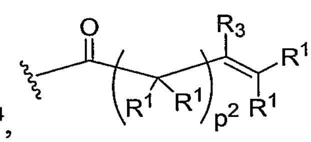
B is 

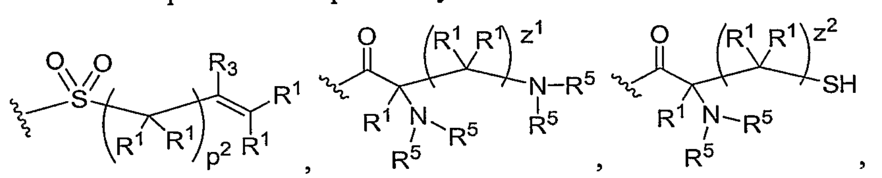


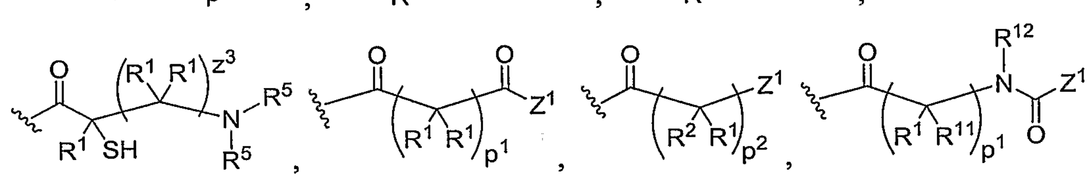


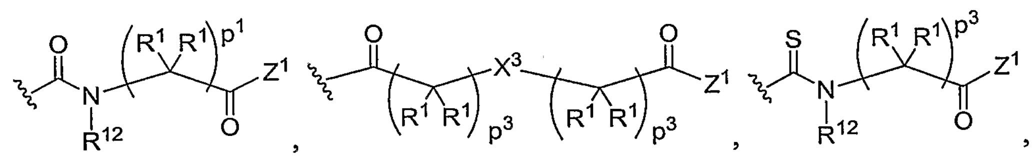


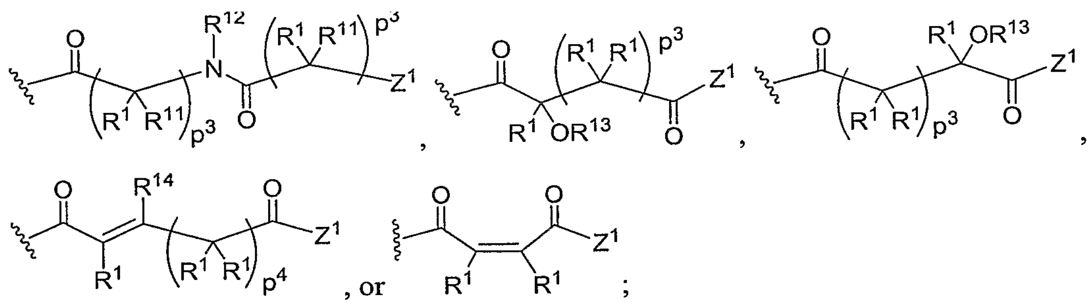
 , or  ;

Y^1 represents independently for each occurrence R^4, A^4, 

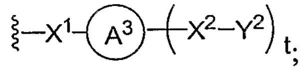


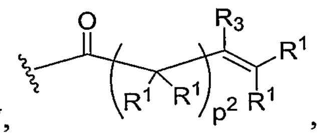


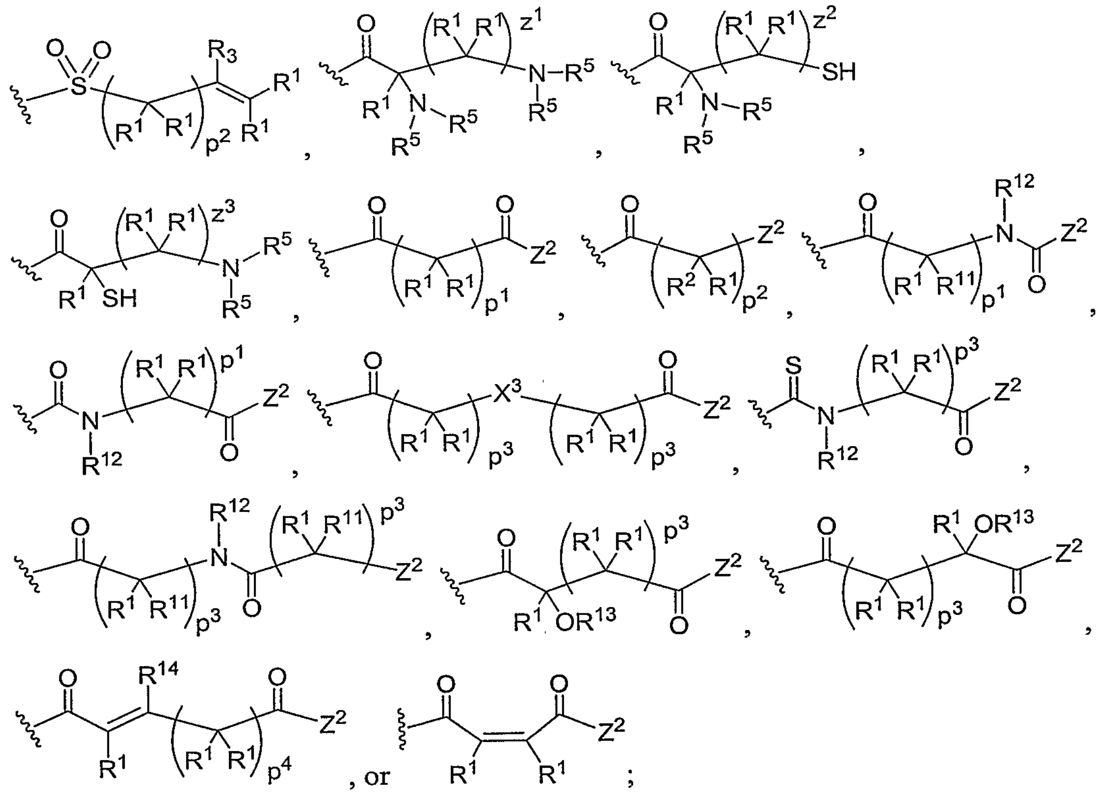




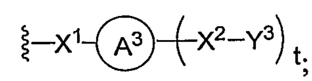
Z^1 represents independently for each occurrence $-X^1-R^4$, E, or

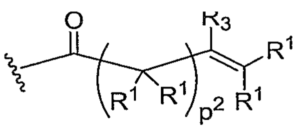


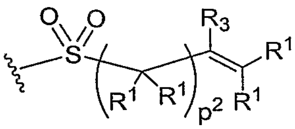
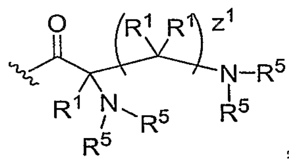
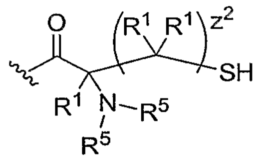
Y^2 represents independently for each occurrence R^5, A^4, 

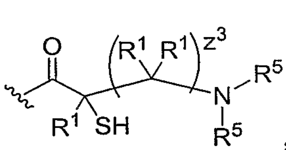
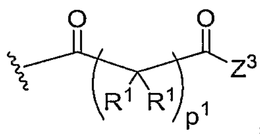
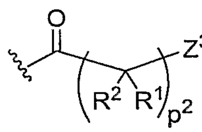
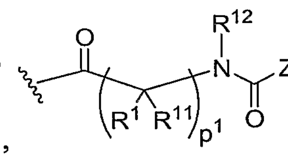


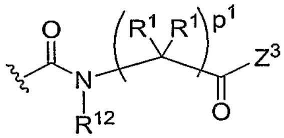
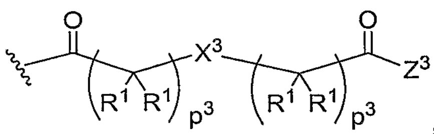
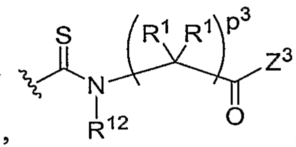
Z^2 represents independently for each occurrence $-X^1-R^5$, E, or

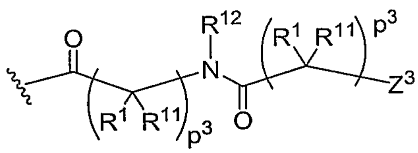
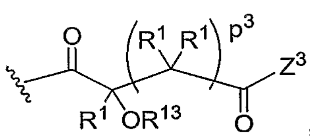
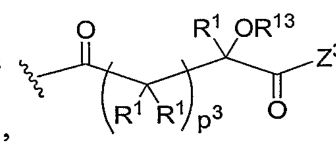


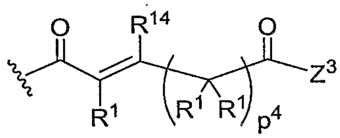
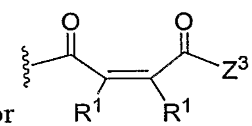
Y^3 represents independently for each occurrence R^6, A^4, ,

, , ,

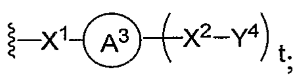
, , , ,

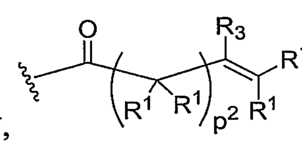
, , ,

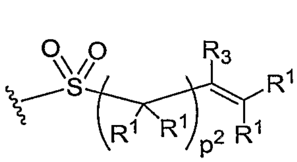
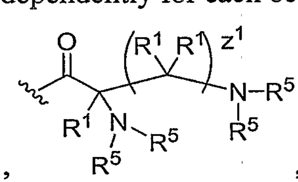
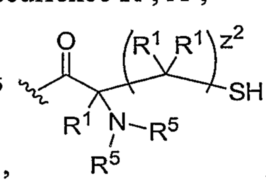
, , ,

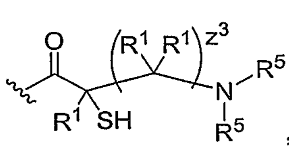
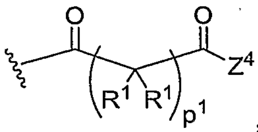
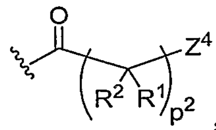
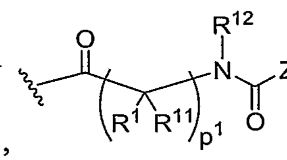
, or ;

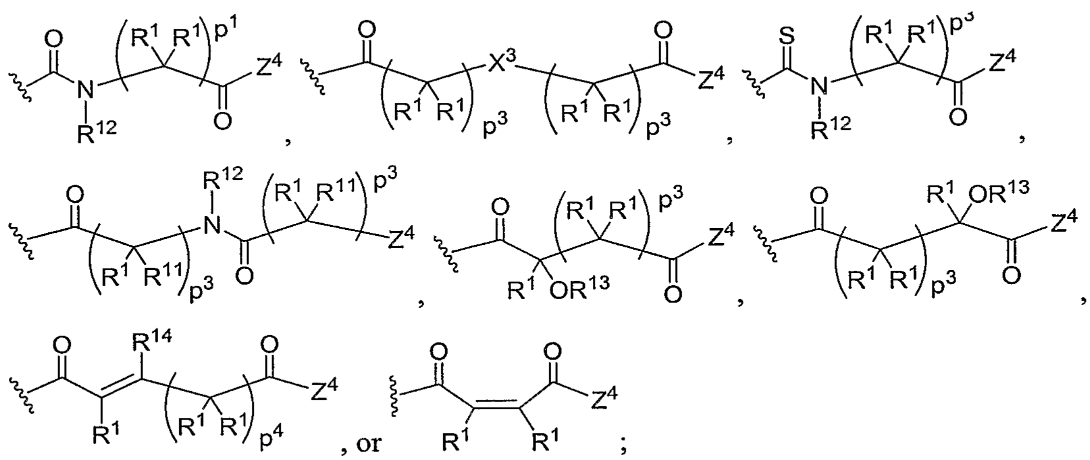
Z^3 represents independently for each occurrence $-X^1-R^6$, E, or

;

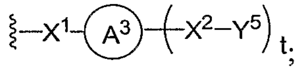
Y^4 represents independently for each occurrence R^7, A^4, ,

, , ,

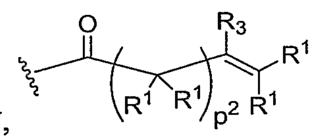
, , , ,

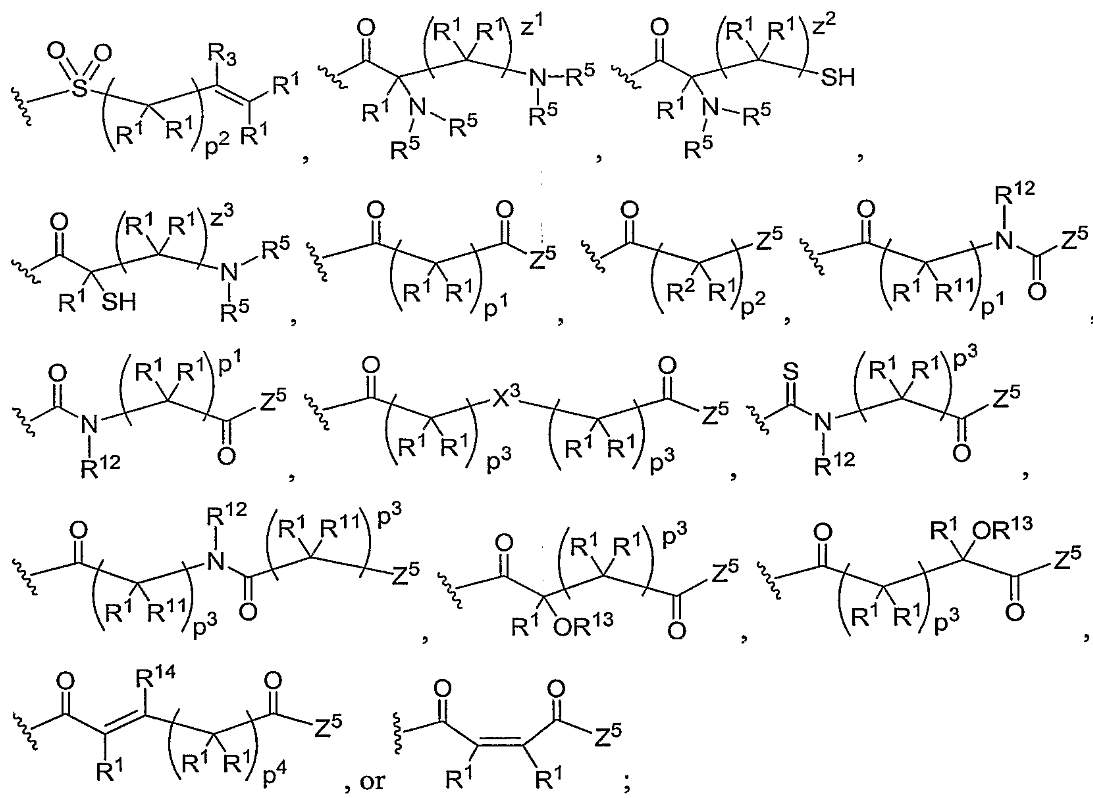


Z^4 represents independently for each occurrence $-X^1-R^7$, E, or

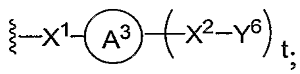


Y^5 represents independently for each occurrence R^8, A^4,

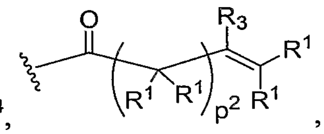


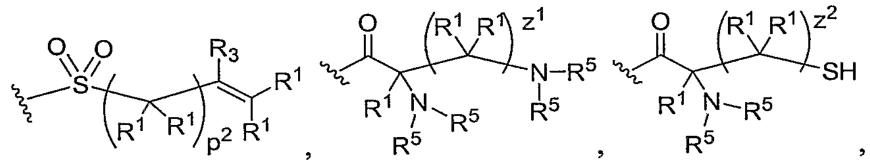


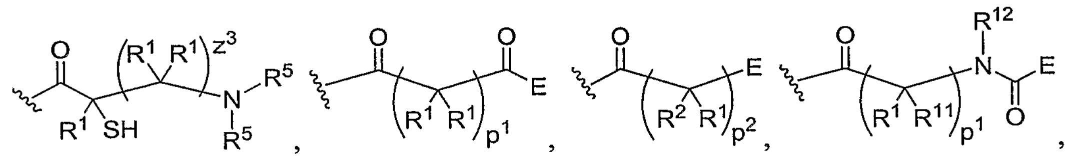
Z^5 represents independently for each occurrence $-X^1-R^8$, E, or

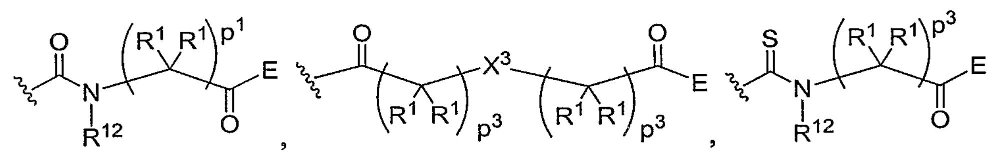


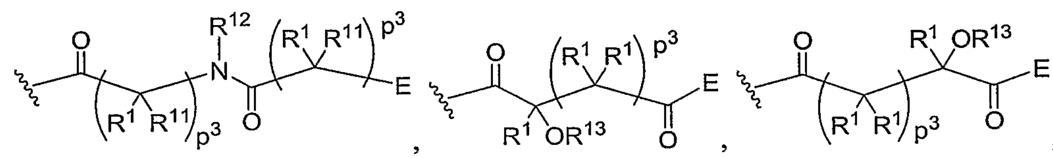
Y^6 represents independently for each occurrence R^9, A^4,

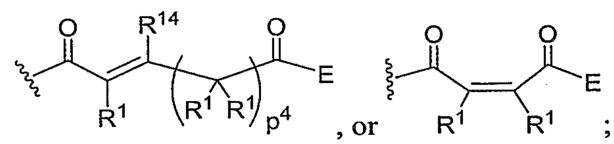












R^1 represents independently for each occurrence H, alkyl, or halogen;

R^2 represents independently for each occurrence H, alkyl, -OH, -N(R^{10})$_2$, -SH, hydroxyalkyl, or -[C(R^1)$_2$]$_d$$R^{16}$;

R^3 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^4, R^5, R^6, R^7, R^8, and R^9 are H;

R^{10} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{11} represents independently for each occurrence H, -OH, -N(R^{10})$_2$, -SH, alkyl, hydroxyalkyl, or -[C(R^1)$_2$]$_d$$R^{16}$;

R^{12} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{13} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{14} represents independently for each occurrence H, alkyl, or $-CO_2R^{10}$;

R^{15} represents independently for each occurrence H, alkyl, or $-OR^{10}$;

R^{16} represents independently for each occurrence phenyl, hydroxyphenyl, pyrrolidyl, imidazolyl, indolyl, $-N(R^{10})_2$, -SH, -S-alkyl, $-CO_2R^{10}$, $-C(O)N(R^{10})_2$, or $-C(NH_2)N(R^{10})_2$;

d represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

n represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

p^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7; or 8;

p^2 represents independently for each occurrence 0, 1, 2, 3, or 4;

p^3 represents independently for each occurrence 1, 2, or 3;

p^4 represents independently for each occurrence 0, 1, 2, or 3;

t represents independently for each occurrence 2, 3, 4, or 5 in accord with the rules of valence;

v^1 and v^2 each represent independently for each occurrence 2, 3, or 4;

w^1 and w^2 each represent independently for each occurrence an integer from about 5 to about 700, inclusive;

x is 1, 2, or 3;

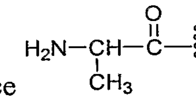
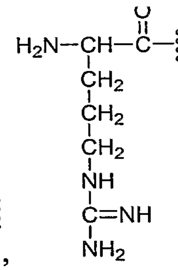
y is 0, 1, 2, 3, 4, or 5;

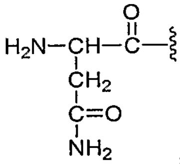
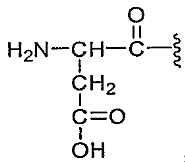
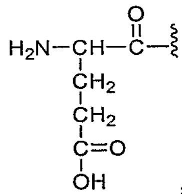
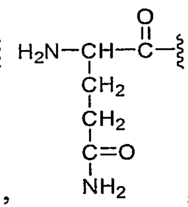
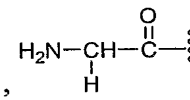
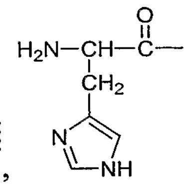
z^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

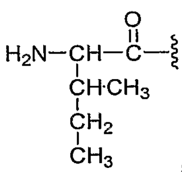
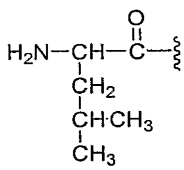
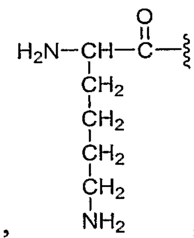
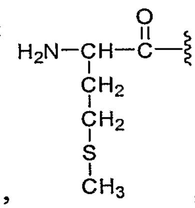
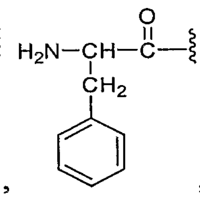
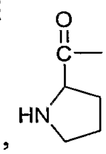
z^2 and z^3 each represent independently for each occurrence 1, 2, 3, 4, or 5;

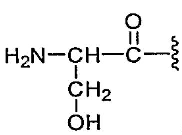
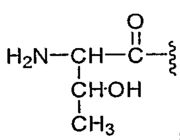
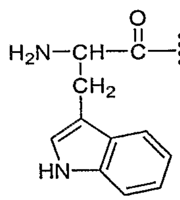
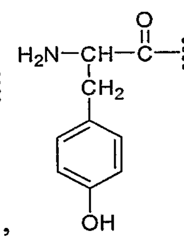
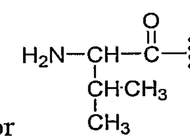
X^1 and X^2 each represent independently for each occurrence O or $-N(R^{10})-$;

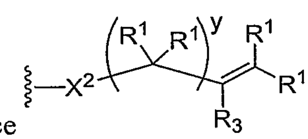
X^3 represents independently for each occurrence O, $N(R^{10})$, or $C(R^{15})(CO_2R^{10})$;

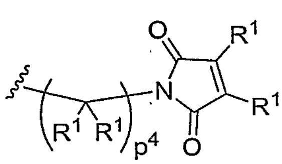
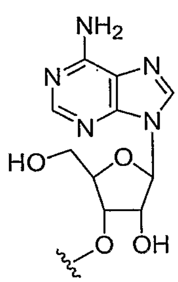
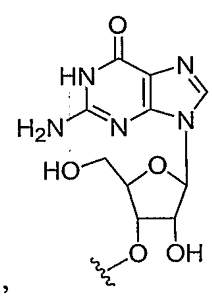
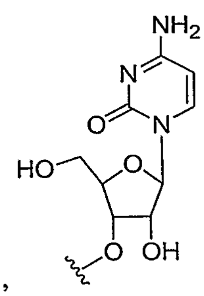
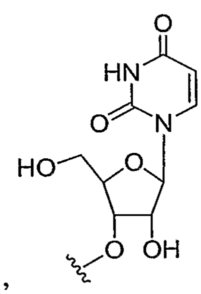
A^4 represents independently for each occurrence  ,  ,

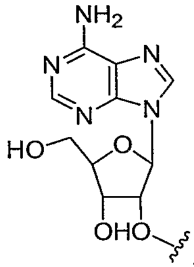
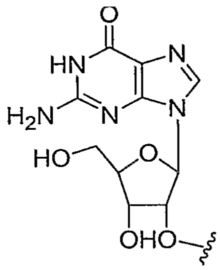
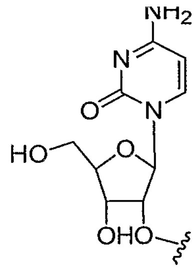
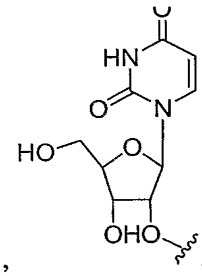
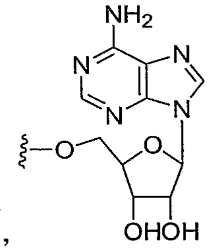
 ,  ,  ,  ,  ,  ,

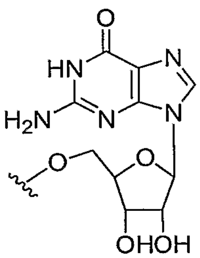
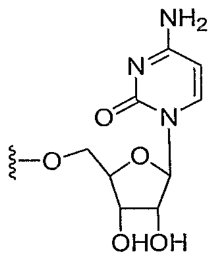
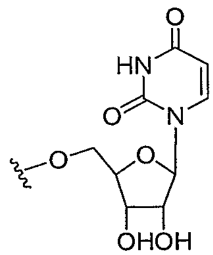
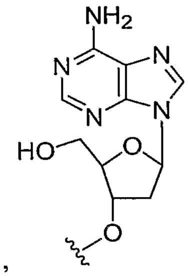
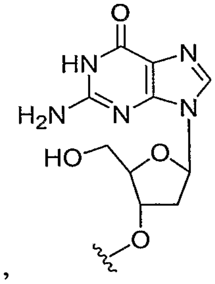
 ,  ,  ,  ,  ,  ,

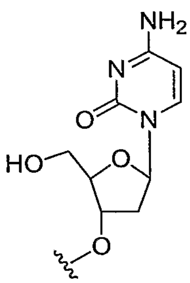
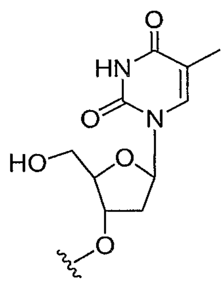
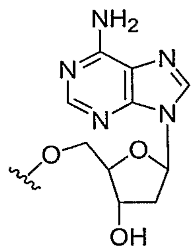
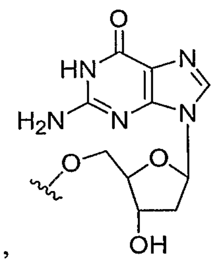
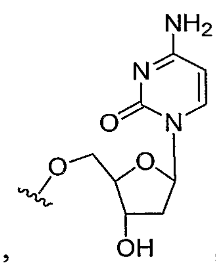
 ,  ,  ,  , or  ;

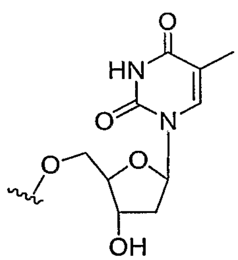
E represents independently for each occurrence  ,

 ,  ,  ,  ,  ,

, , , , ,

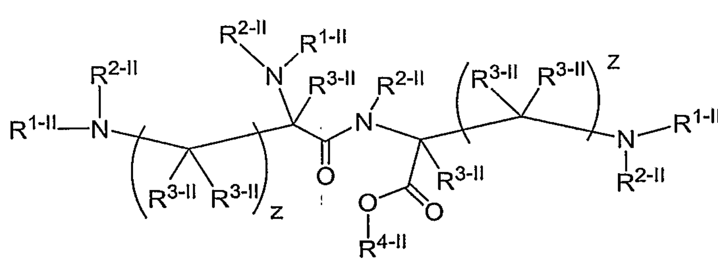
, , , , ,

, , , , , or

 ; and

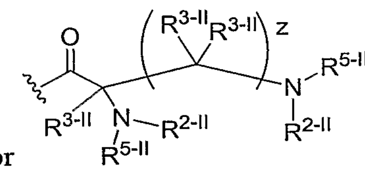
provided that R^4 only occurs once, R^5 only occurs once, R^6 only occurs once, R^7 only occurs once, R^8 only occurs once, and R^9 only occurs once;

said formula **II** is represented by:



II

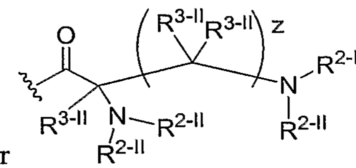
wherein

$R^{1\text{-}II}$ represents independently for each occurrence H or  ;

$R^{2\text{-}II}$ represents independently for each occurrence H or alkyl;

$R^{3\text{-}II}$ represents independently for each occurrence H, halogen, or alkyl;

$R^{4\text{-}II}$ represents independently for each occurrence alkyl, aryl, or aralkyl;

$R^{5\text{-}II}$ represents independently for each occurrence H or  ;

and

z represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8; and

said formula **III** is represented by:

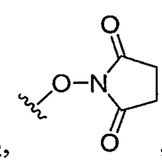
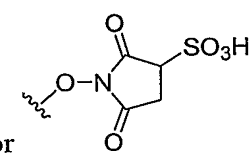
$$R^{1\text{-}III}—B^{1\text{-}III}—R^{1\text{-}III}$$

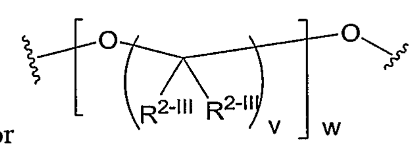
III

wherein

$R^{1\text{-}III}$ is $-(C(R^{2\text{-}III})_2)_xC(O)H$, $-C(O)(C(R^{2\text{-}III})_2)_yC(O)H$, $-(C(R^{2\text{-}III})_2)_xC(O)R^{3\text{-}III}$, or $-C(O)(C(R^{2\text{-}III})_2)_yC(O)R^{3\text{-}III}$;

$R^{2\text{-}III}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}III}$ is fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

$B^{1\text{-}III}$ is alkyl diradical, heteroalkyl diradical, or  ;

x represents independently for each occurrence 0, 1, 2, 3, 4, 5, 6, 7, or 8;

y represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

v represents independently for each occurrence 2, 3, or 4; and

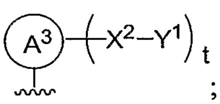
w is an integer in the range of about 5 to about 1000, inclusive; and

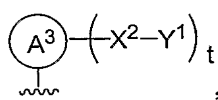
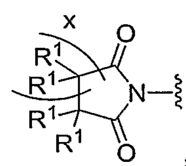
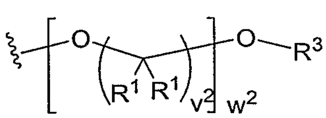
said formula **IV** is represented by:

$$A^1—X^1—B—X^1—A^2$$

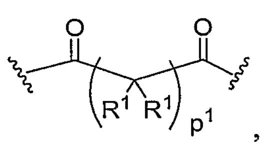
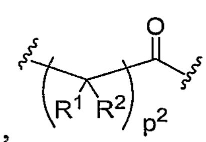
IV

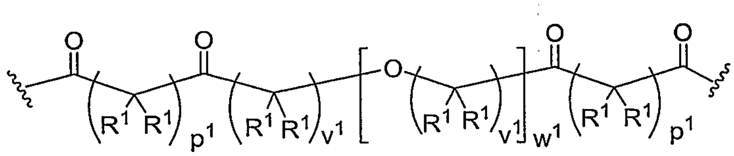
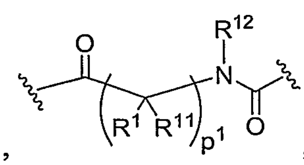
wherein

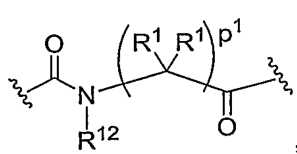
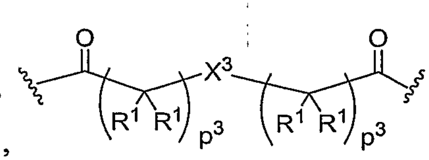
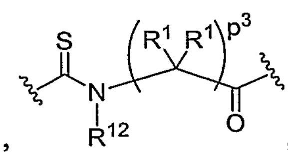
A^1 is  ;

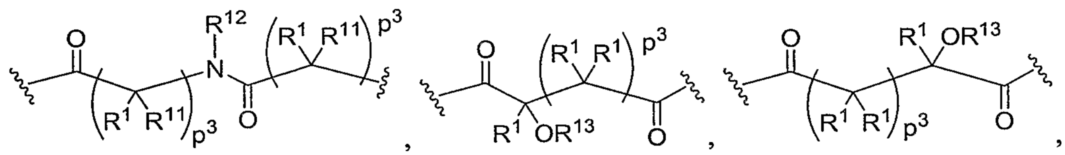
A^2 is alkyl, aryl, aralkyl,r -Si(R^3)$_3$,  ,  , or  ;

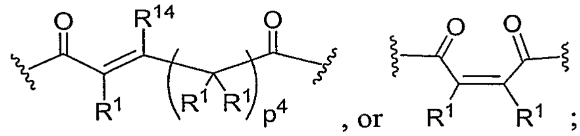
A^3 represents independently for each occurrence alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, heteroaryl, or aralkyl;

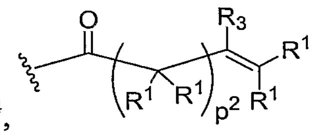
B is  ,  ,

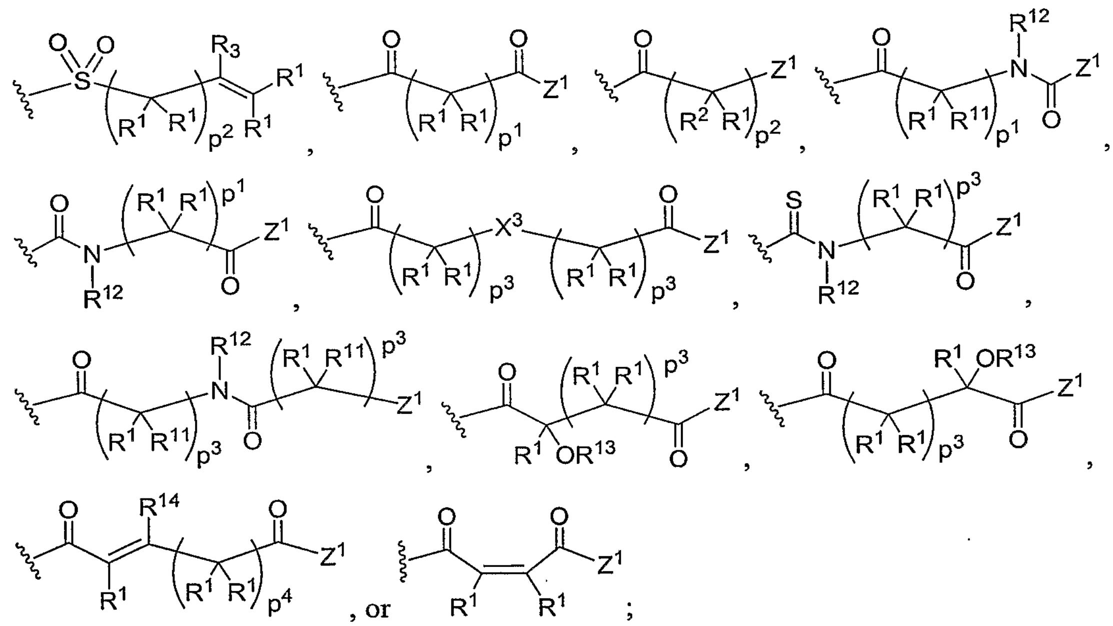
 ,  ,

 ,  ,  ,

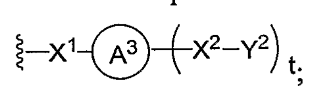


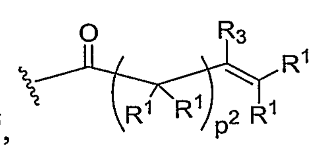


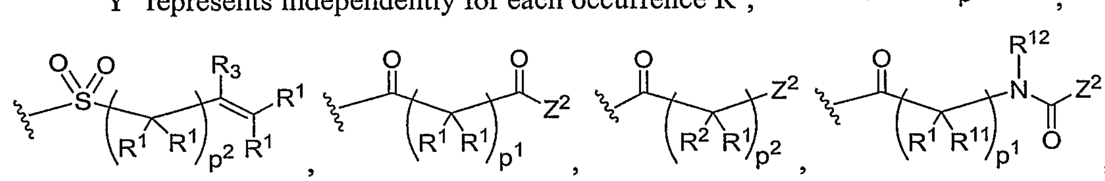
Y^1 represents independently for each occurrence R^4, 

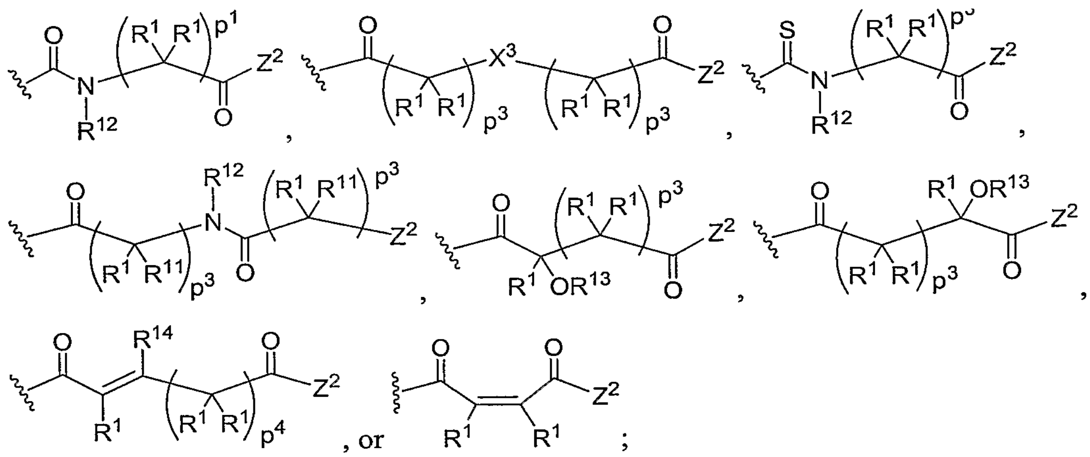


Z^1 represents independently for each occurrence $-X^1-R^4$, E, or

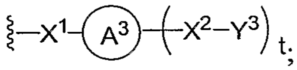


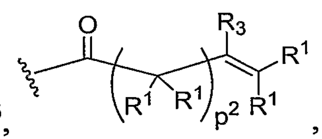
Y^2 represents independently for each occurrence R^5, 

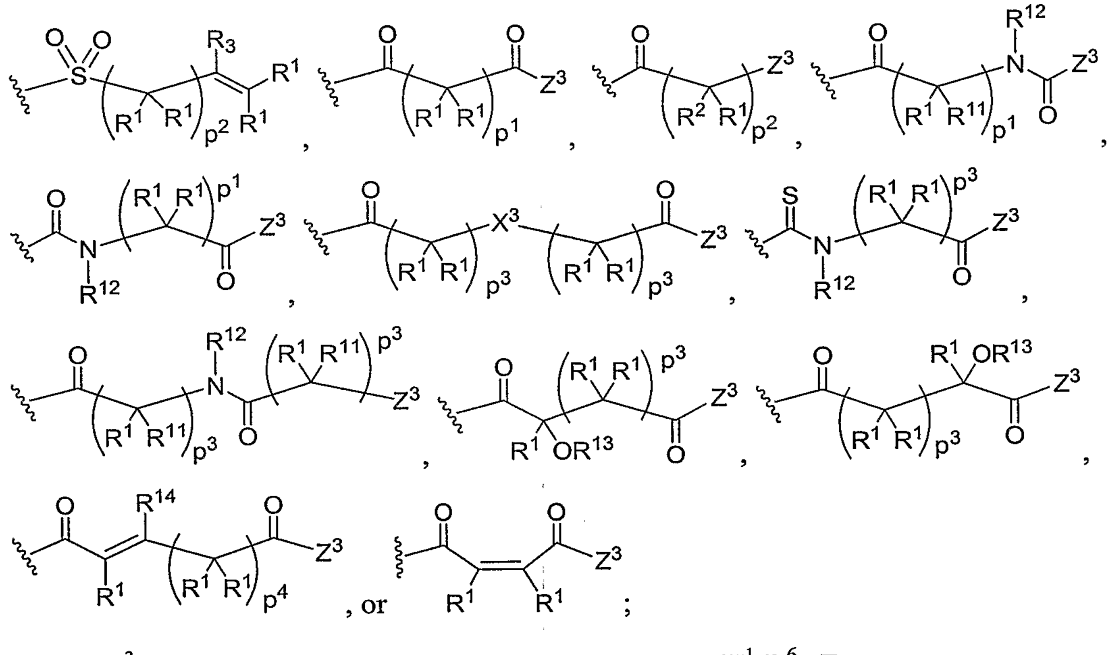




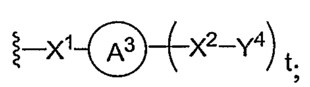
Z^2 represents independently for each occurrence $-X^1-R^5$, E, or

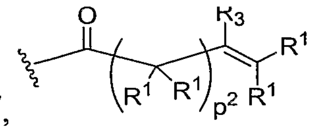


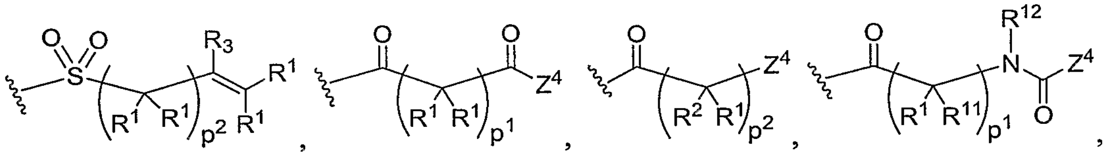
Y^3 represents independently for each occurrence R^6, 

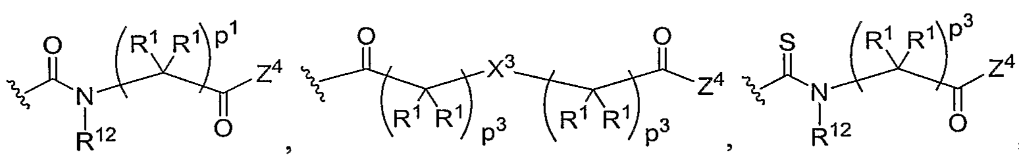


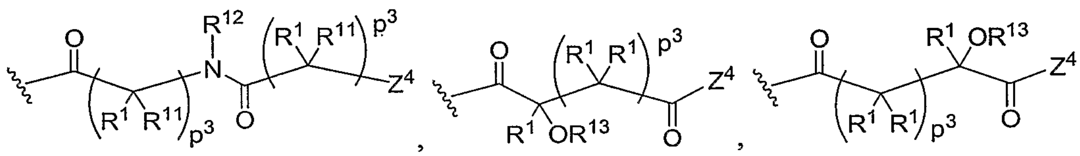
Z^3 represents independently for each occurrence $-X^1-R^6$, E, or

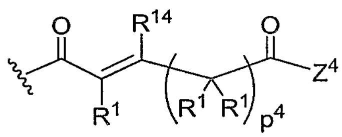
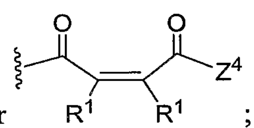


Y^4 represents independently for each occurrence R^7,  ,

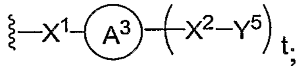


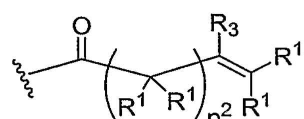


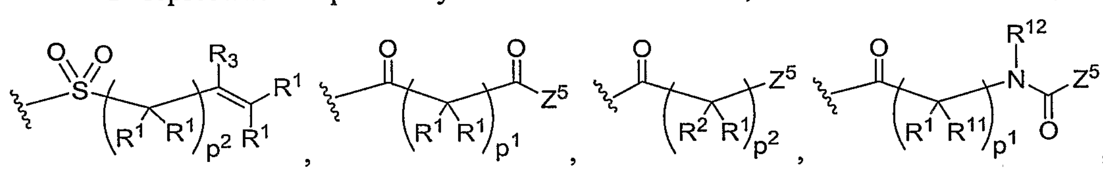


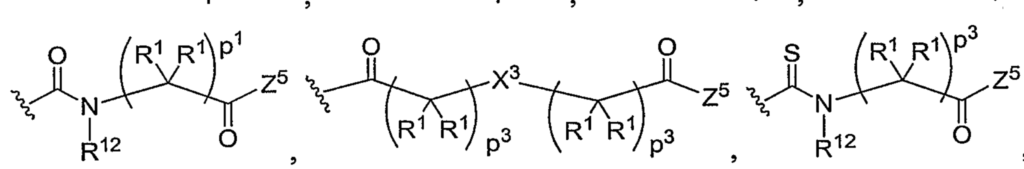
 , or  ;

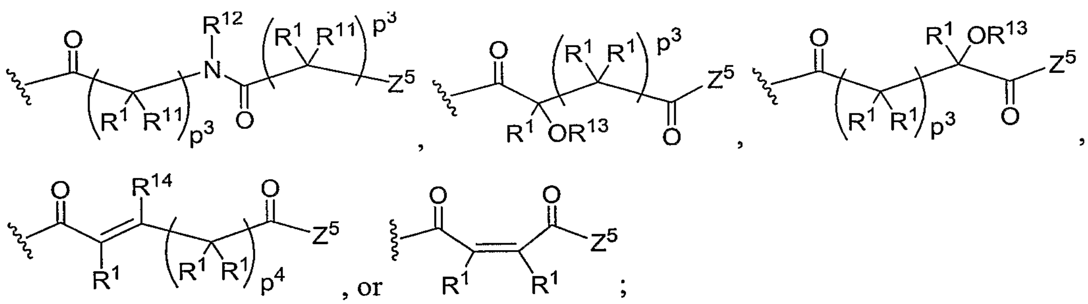
Z^4 represents independently for each occurrence $-X^1-R^7$, E, or

 ;

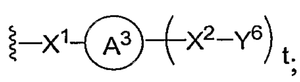
Y^5 represents independently for each occurrence R^8,  ,

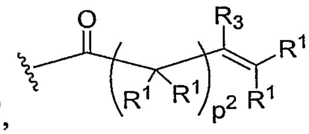


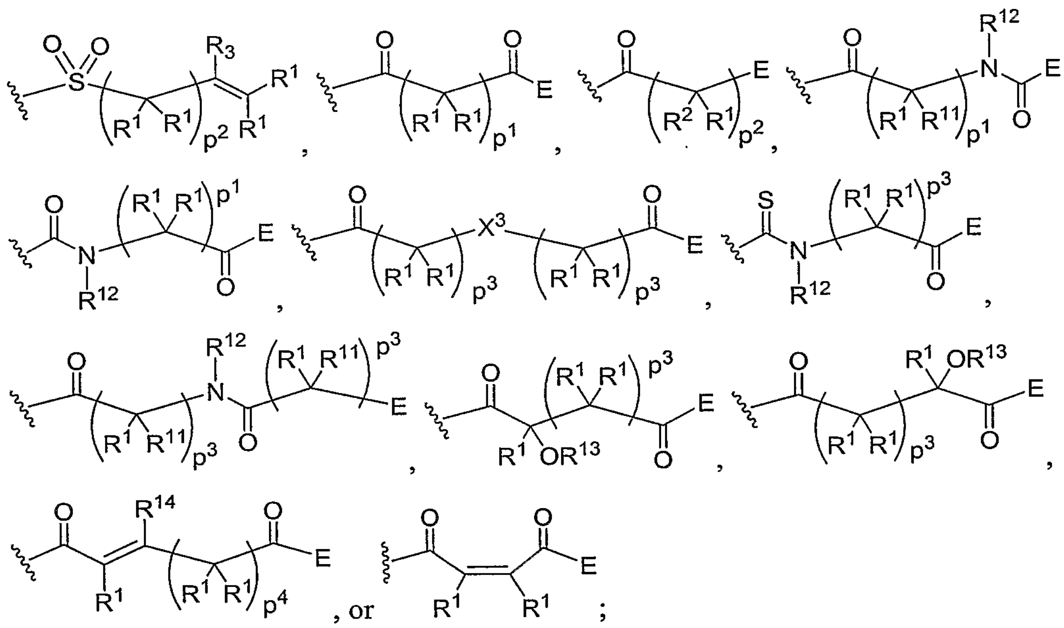




Z^5 represents independently for each occurrence $-X^1-R^8$, E, or



Y^6 represents independently for each occurrence R^9, 



R^1 represents independently for each occurrence H, alkyl, or halogen;

R^2 represents independently for each occurrence H, alkyl, -OH, $-N(R^{10})_2$, -SH, hydroxyalkyl, or $-[C(R^1)_2]_dR^{16}$;

R^3 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^4, R^5, R^6, R^7, R^8, and R^9 are H;

R^{10} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{11} represents independently for each occurrence H, -OH, -N(R^{10})$_2$, -SH, alkyl, hydroxyalkyl, or -[C(R^1)$_2$]$_d$$R^{16}$;

R^{12} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{13} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{14} represents independently for each occurrence H, alkyl, or -CO_2R^{10};

R^{15} represents independently for each occurrence H, alkyl, or -OR^{10};

R^{16} represents independently for each occurrence phenyl, hydroxyphenyl, pyrrolidyl, imidazolyl, indolyl, -N(R^{10})$_2$, -SH, -S-alkyl, -CO_2R^{10}, -C(O)N(R^{10})$_2$, or -C(NH_2)N(R^{10})$_2$;

n represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

p^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7; or 8;

p^2 represents independently for each occurrence 0, 1, 2, 3, or 4;

p^3 represents independently for each occurrence 1, 2, or 3;

p^4 represents independently for each occurrence 0, 1, 2, or 3;

d represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

t represents independently for each occurrence 2, 3, 4, or 5 in accord with the rules of valence;

v^1 and v^2 each represent independently for each occurrence 2, 3, or 4;

w^1 and w^2 each represent independently for each occurrence an integer from about 5 to about 700, inclusive;

x is 1, 2, or 3;

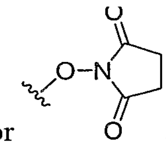
y is 0, 1, 2, 3, 4, or 5;

z^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

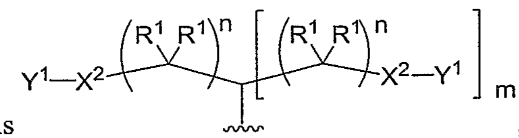
z^2 and z^3 each represent independently for each occurrence 1, 2, 3, 4, or 5;

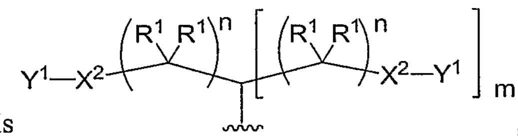
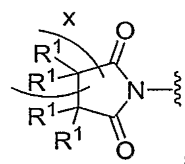
X^1 and X^2 each represent independently for each occurrence O or -N(R^{10})-;

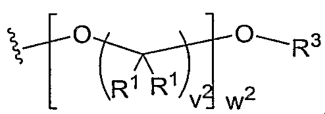
X^3 represents independently for each occurrence O, N(R^{10}), or C(R^{15})(CO_2R^{10}); and

E represents independently for each occurrence H, $-[C(R^1)_2]_nC(O)H$, or  .

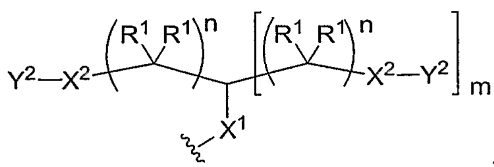
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is ultraviolet light, visible light, a compound of formula **II**, a compound of formula **III**, or an oxidizing agent.

In certain instances, the present invention relates to the aforementioned method, wherein A^1 is  , and m is 1 or 2.

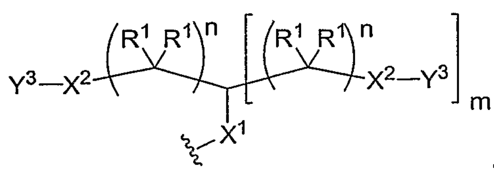
In certain instances, the present invention relates to the aforementioned method, wherein A^2 is  ,  ,

 , or $-Si(R^3)_3$; wherein, m is 1 or 2.

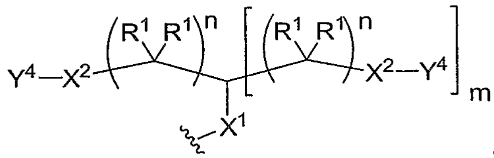
In certain instances, the present invention relates to the aforementioned method, wherein Z^1 represents independently for each occurrence $-X^1-R^4$ or

 , and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^2 represents independently for each occurrence $-X^1-R^5$ or

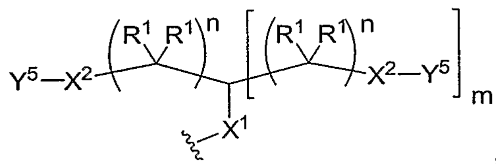
 , and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^3 represents independently for each occurrence $-X^1-R^6$ or



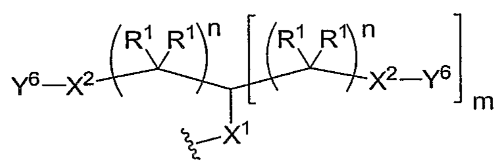
, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^4 represents independently for each occurrence $-X^1-R^7$ or



, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^5 represents independently for each occurrence $-X^1-R^8$ or



, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein X^1 is O.

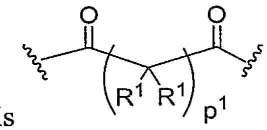
In certain instances, the present invention relates to the aforementioned method, wherein X^1 and X^2 are O.

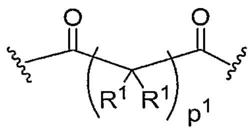
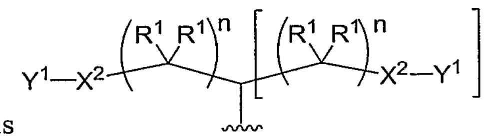
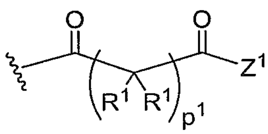
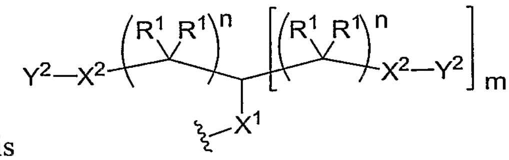
In certain instances, the present invention relates to the aforementioned method, wherein n is 1.

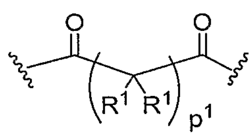
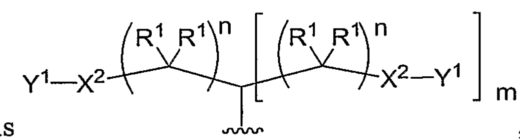
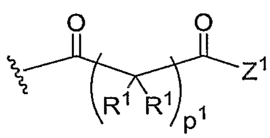
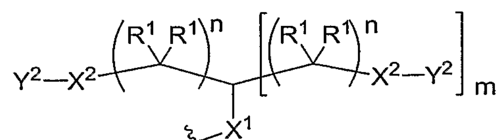
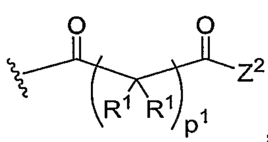
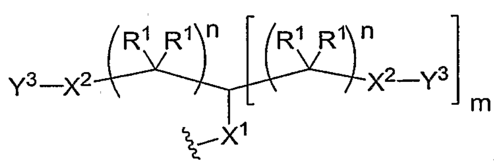
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, 3, or 4.

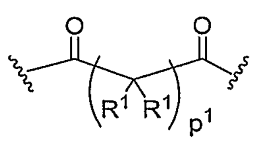
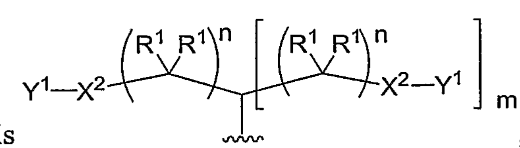
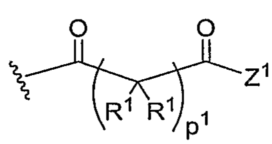
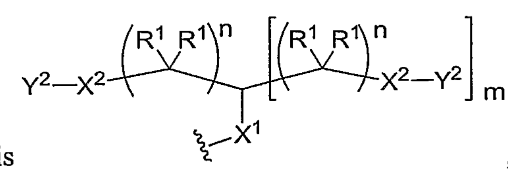
In certain instances, the present invention relates to the aforementioned method, wherein p^2 is 1.

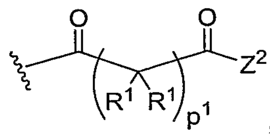
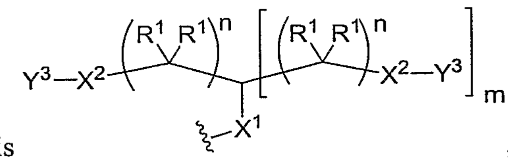
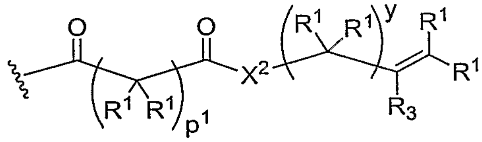
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H.

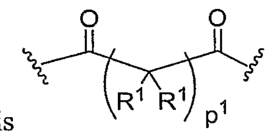
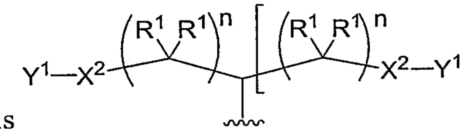
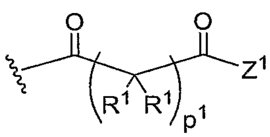
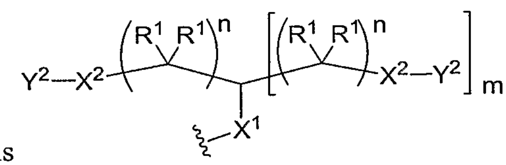
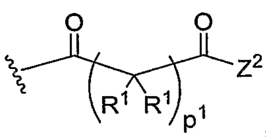
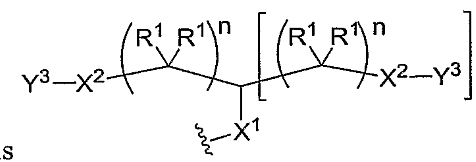
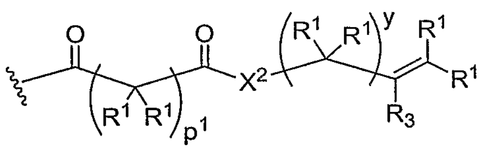
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

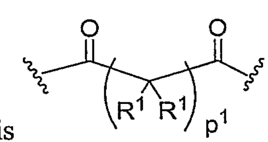
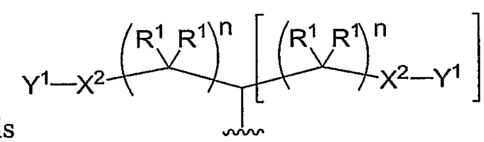
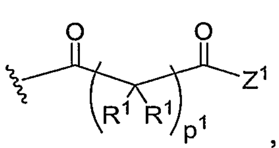
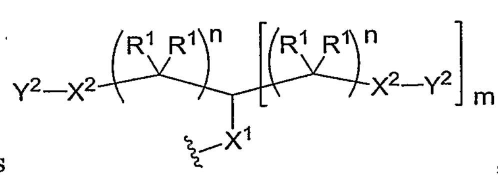
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , and Z^1 is  .

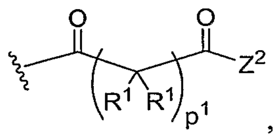
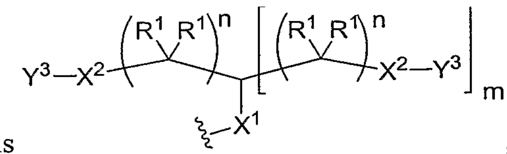
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is  .

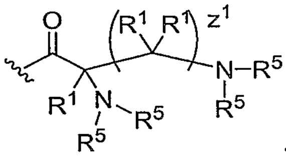
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

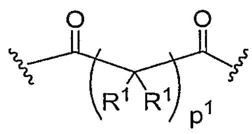
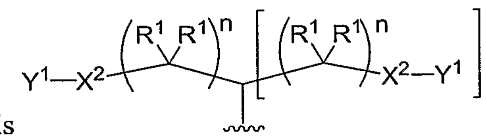
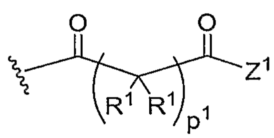
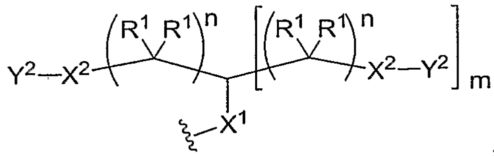
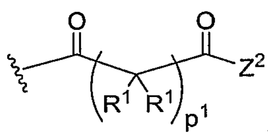
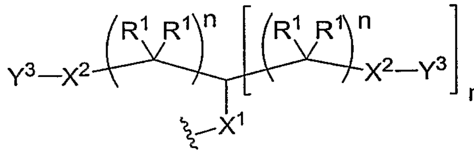
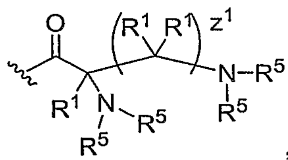
, Z^2 is , and Y^3 is .

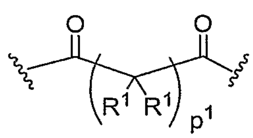
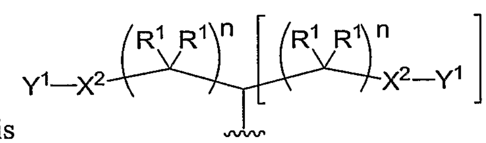
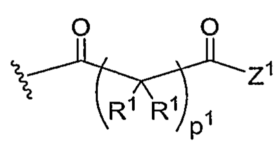
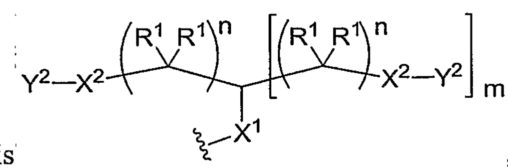
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is ultraviolet light or visible light.

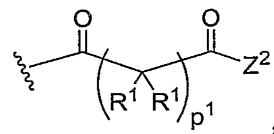
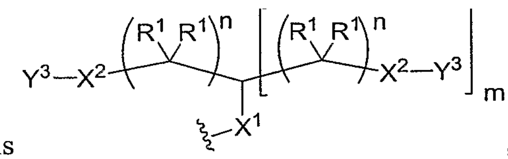
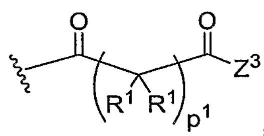
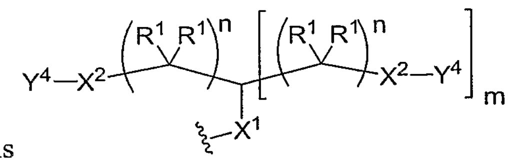
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

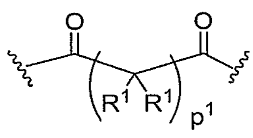
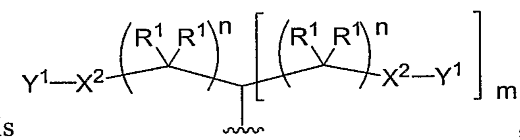
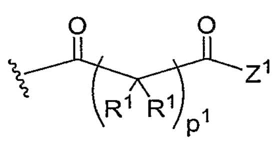
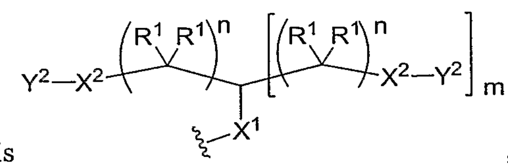
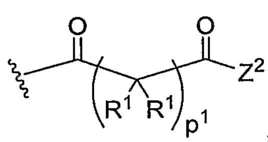
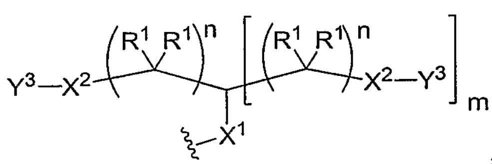
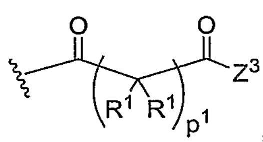
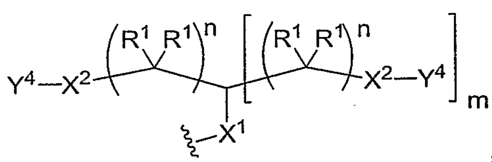
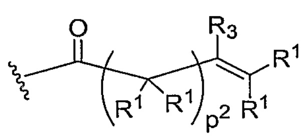
 , Z^2 is  , and Y^3 is

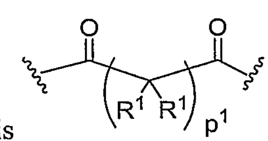
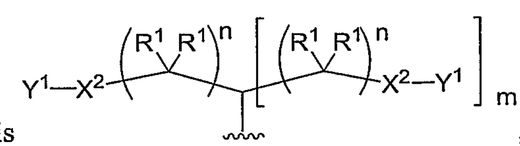
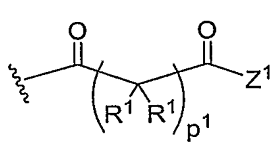
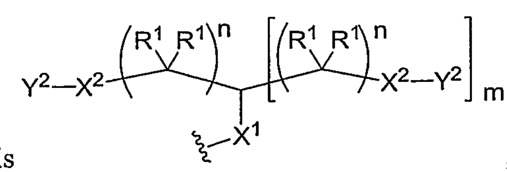
 .

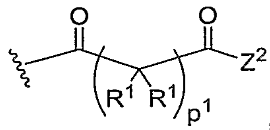
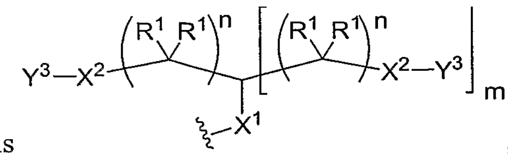
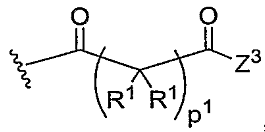
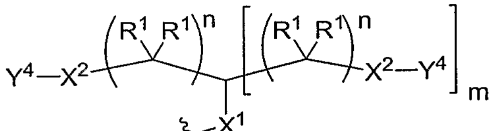
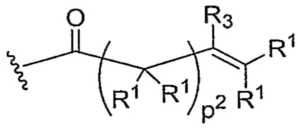
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and said polymerization agent is a compound of formula **III**.

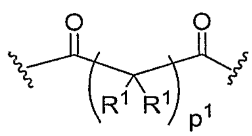
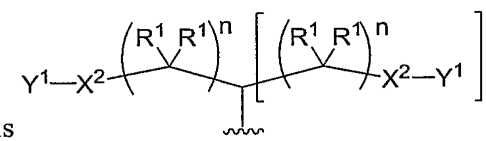
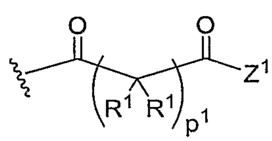
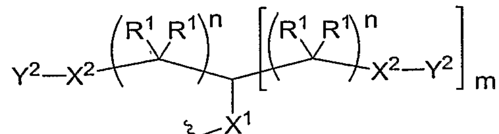
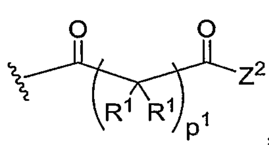
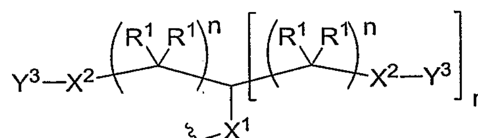
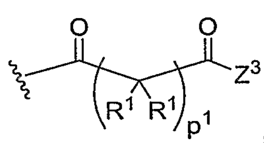
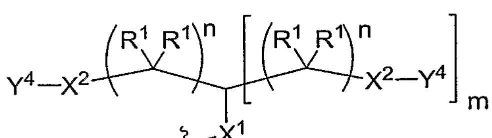
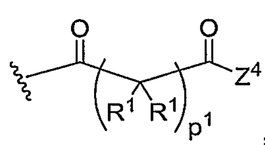
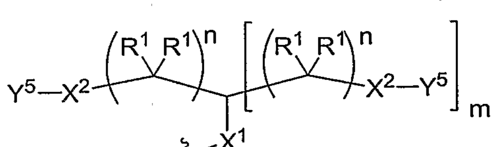
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is

, Z^2 is , Y^3 is , and Z^3 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , and at least about 1/2 of the Y^4 groups are .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

 , Z^2 is  , Y^3 is  , Z^3 is  , at least about 1/2 of the Y^4 groups are  , and said polymerization agent is ultraviolet light or visible light.

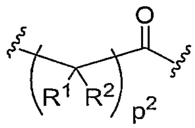
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is  , and Z^4 is  .

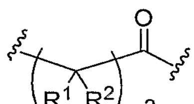
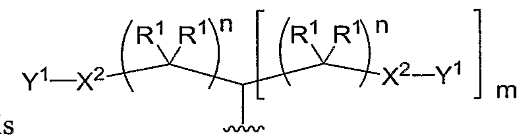
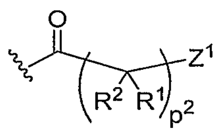
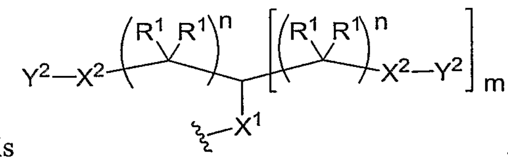
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 1, 2, 3, or 4.

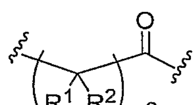
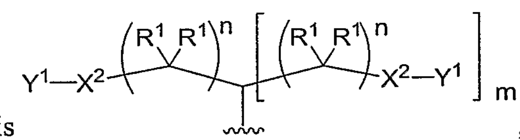
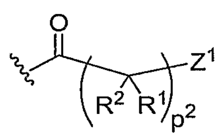
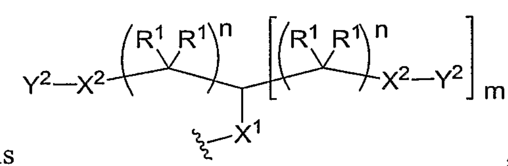
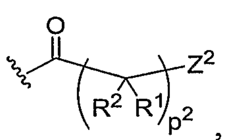
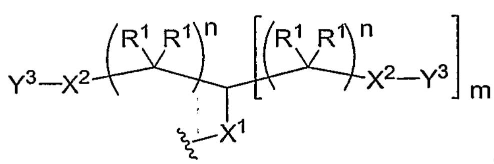
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

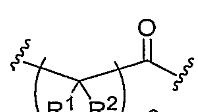
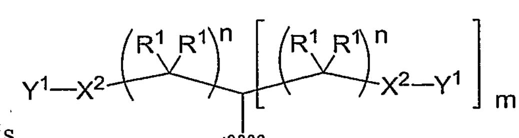
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 4.

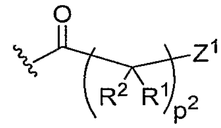
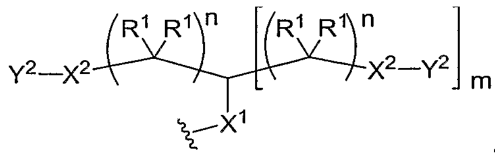
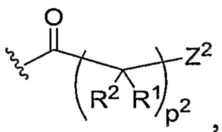
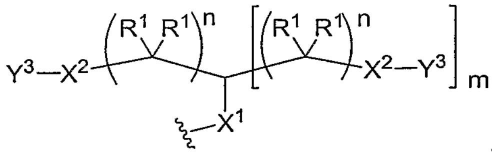
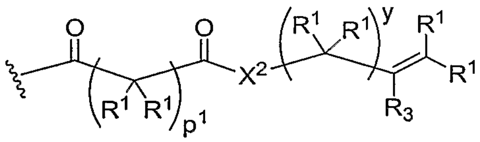
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

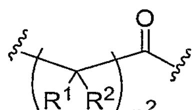
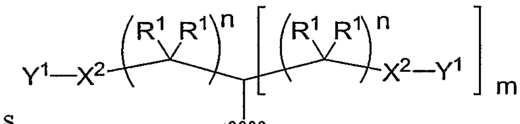
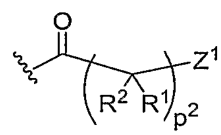
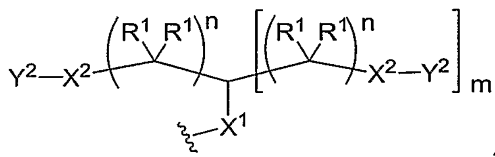
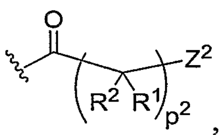
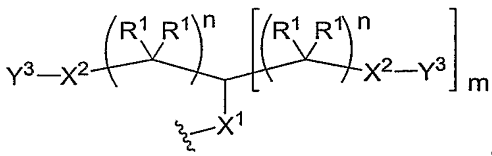
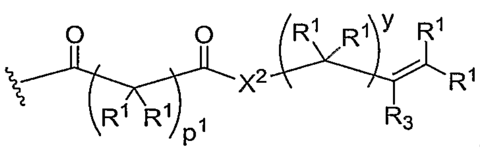
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

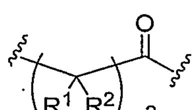
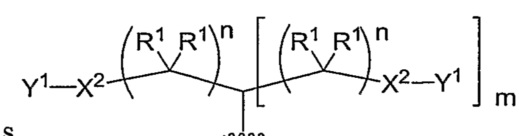
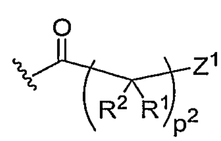
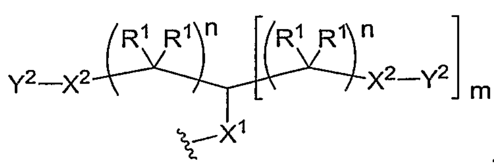
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

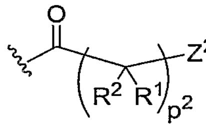
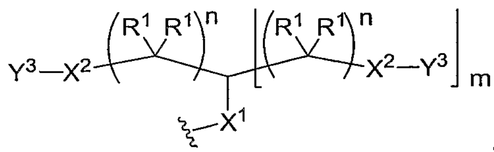
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

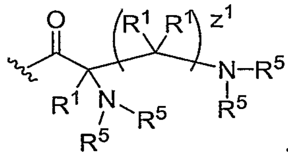
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1

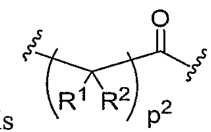
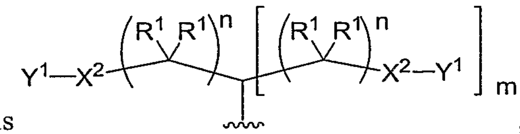
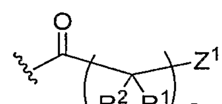
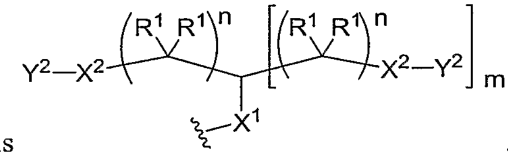
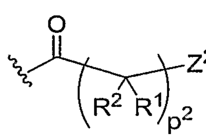
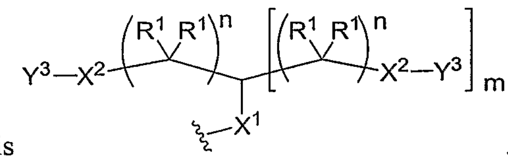
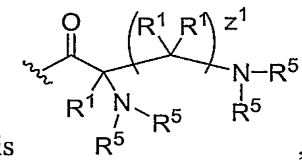
or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

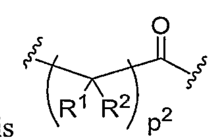
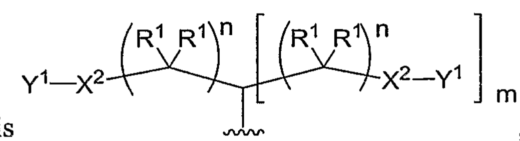
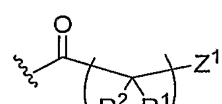
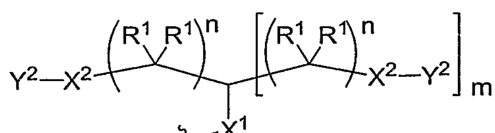
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is ultraviolet light or visible light.

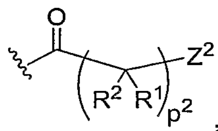
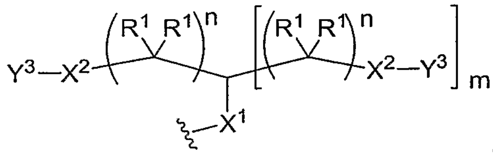
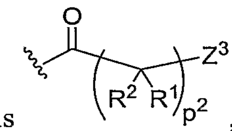
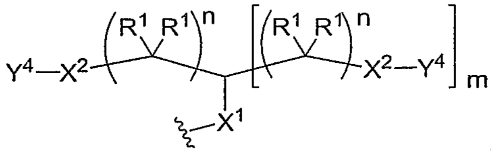
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

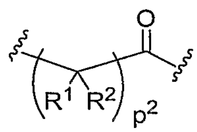
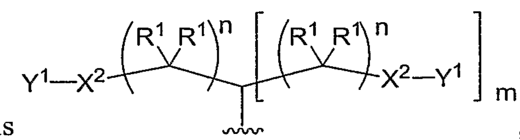
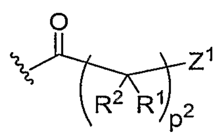
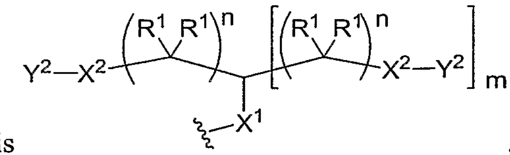
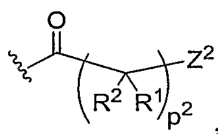
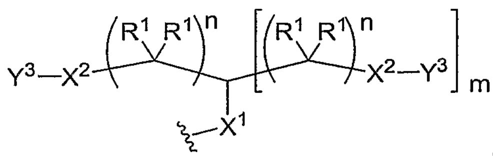
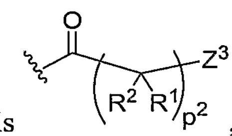
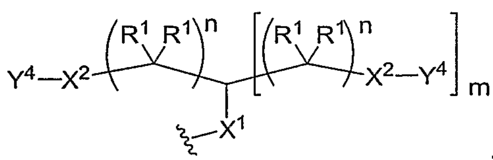
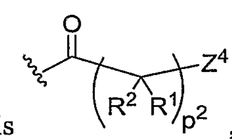
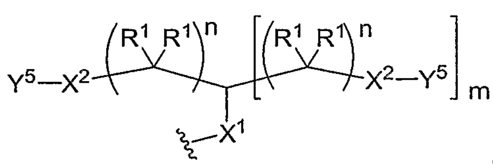
, Z^2 is , and Y^3 is

.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is a compound of formula **III**.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

, Z^2 is , Y^3 is , and Z^3 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , and Z^4 is .

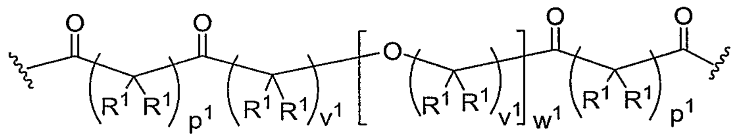
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 1, 2, 3, or 4.

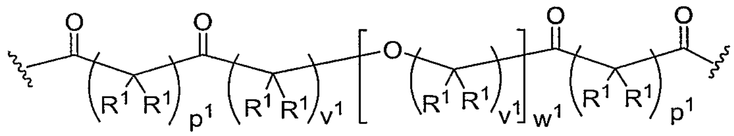
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

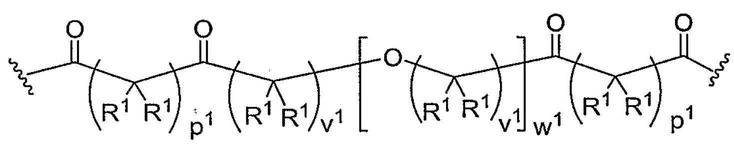
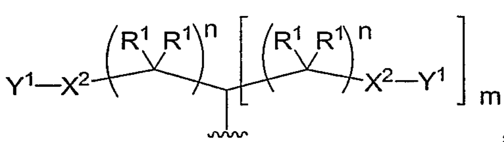
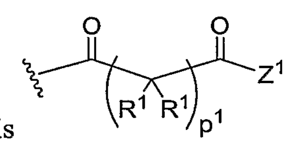
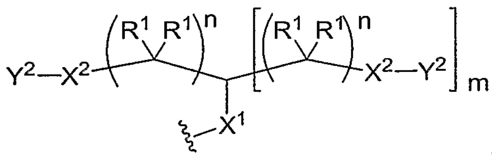
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 4.

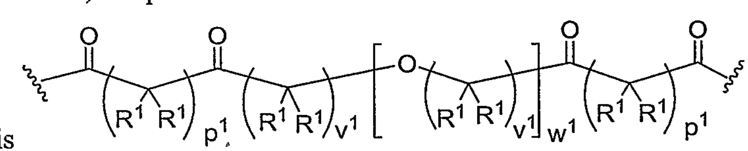
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

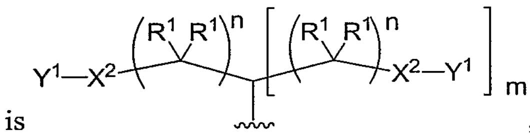
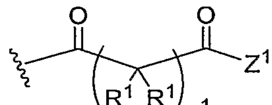
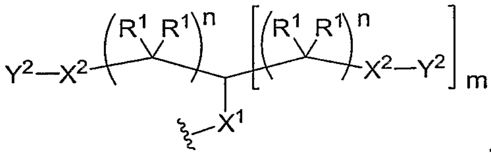
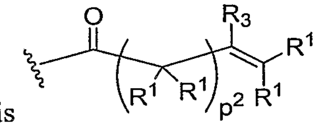
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is $(C_1\text{-}C_3)$alkyl.

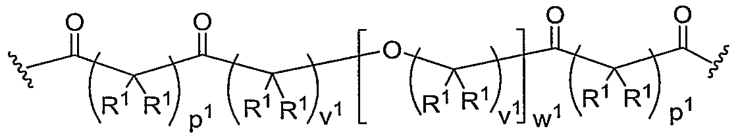
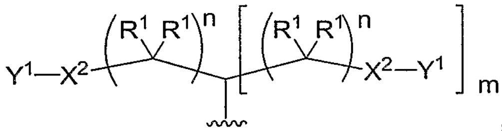
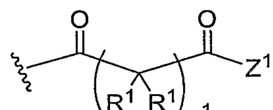
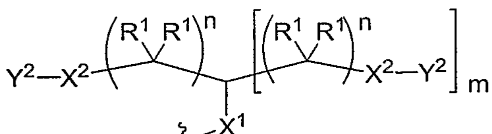
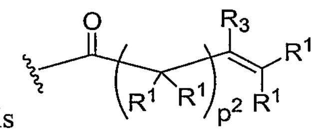
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

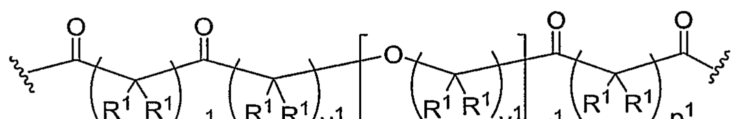
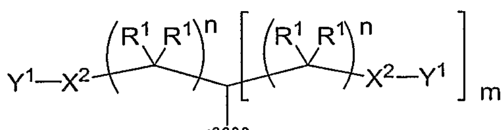
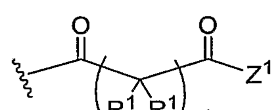
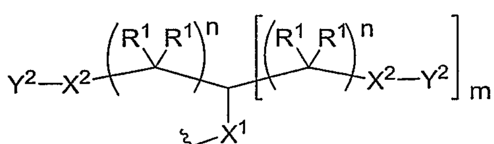
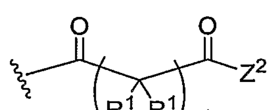
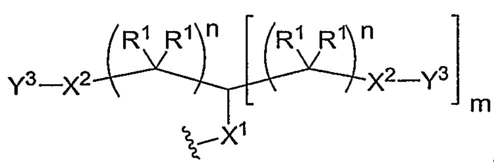
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , and v^1 is 2.

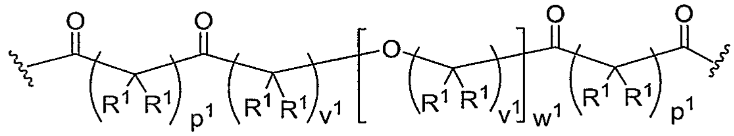
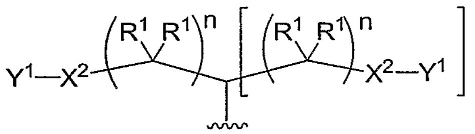
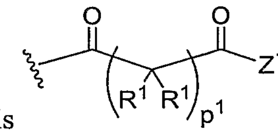
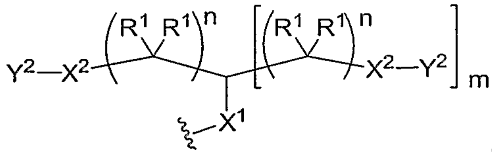
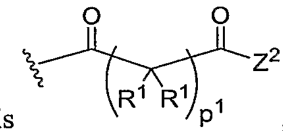
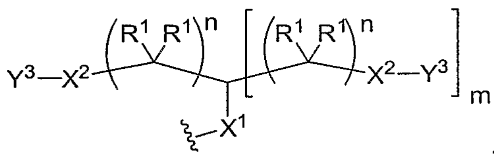
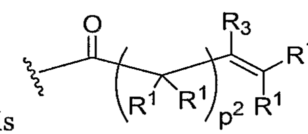
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

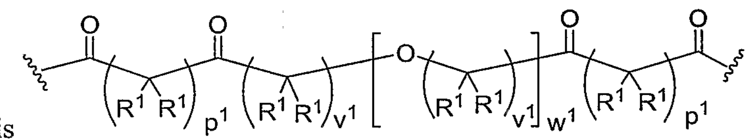
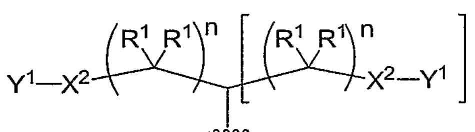
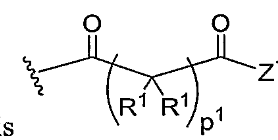
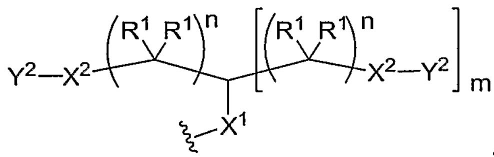
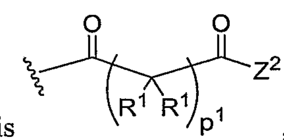
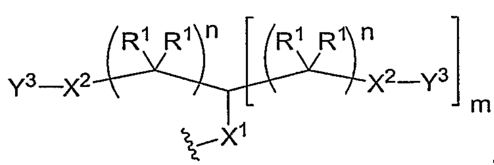
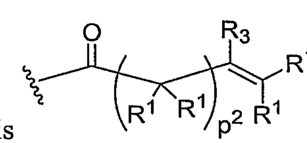
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2

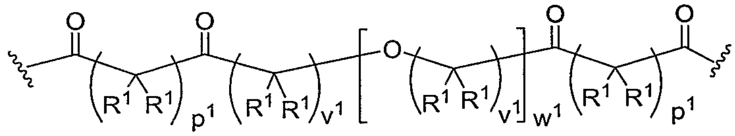
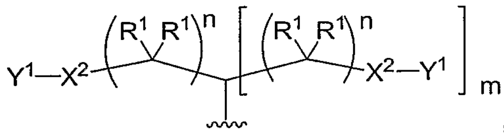
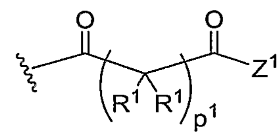
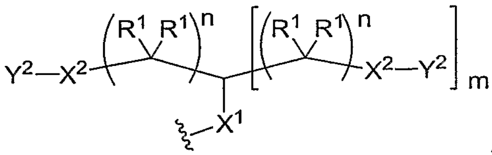
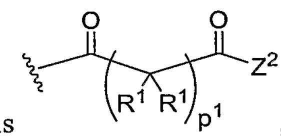
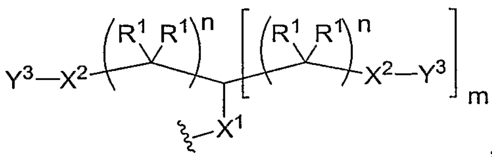
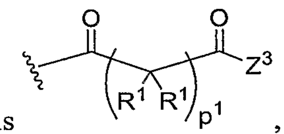
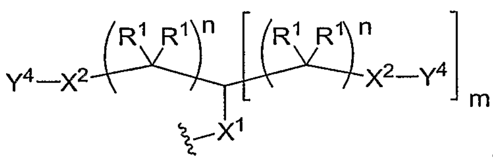
is , m is 1 or 2, Y^1 is , Z^1 is , and Y^2 is .

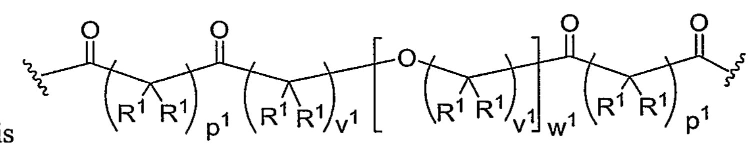
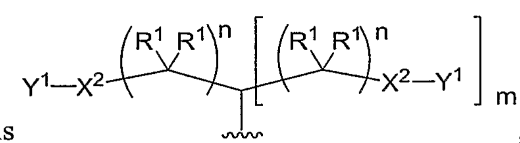
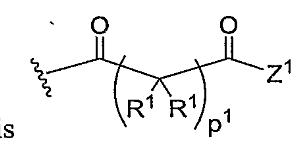
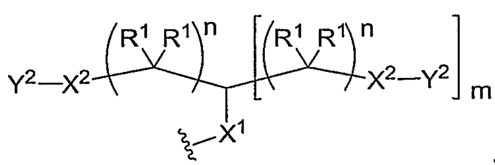
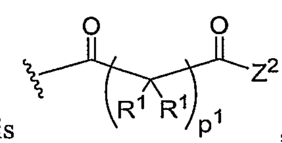
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , and Z^1 is , Y^2 is , and said polymerization agent is ultraviolet light or visible light.

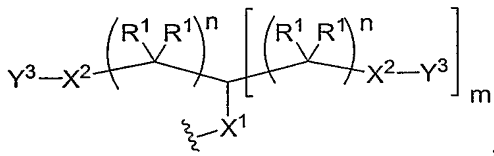
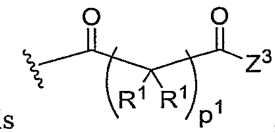
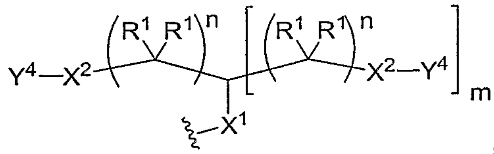
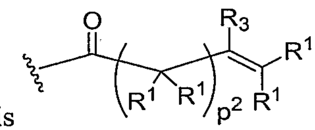
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is .

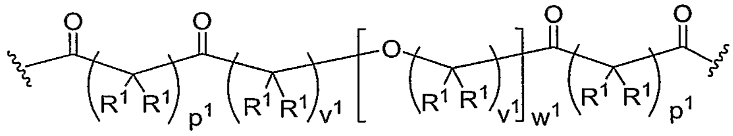
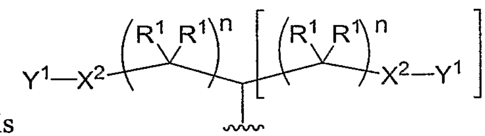
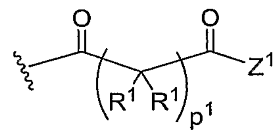
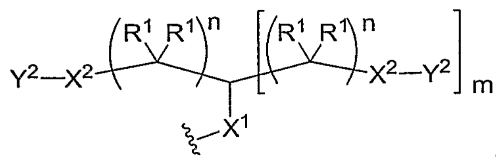
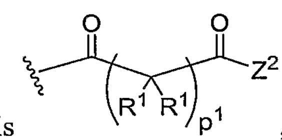
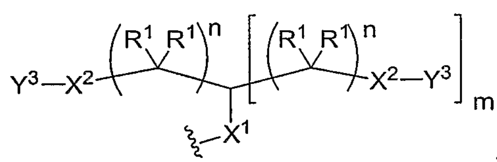
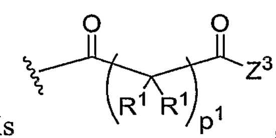
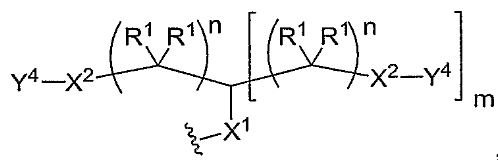
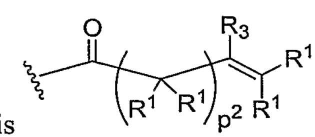
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

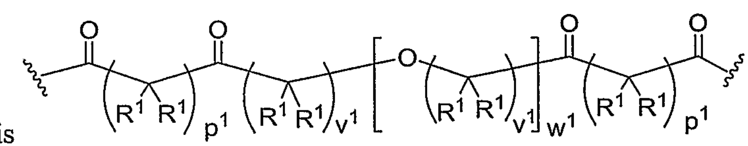
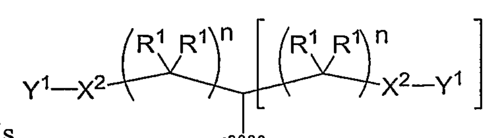
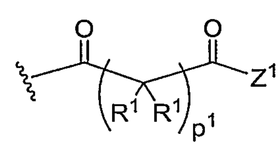
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is ultraviolet light or visible light.

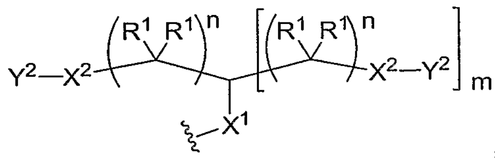
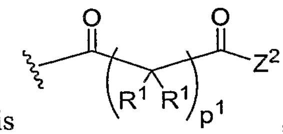
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and Z^3 is .

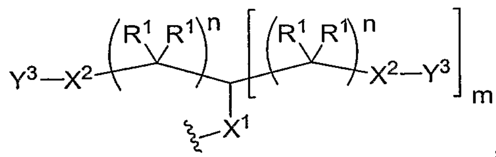
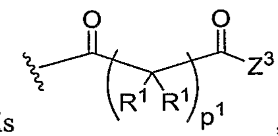
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is

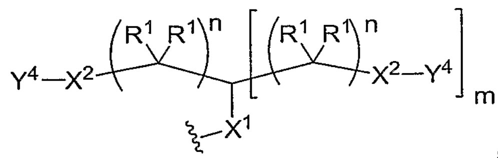
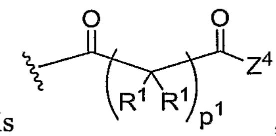
 , Y^3 is  , Z^3 is  , and Y^4 is  .

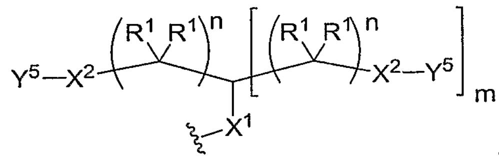
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is  , and said polymerization agent is ultraviolet light or visible light.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is

 , Y^2 is  , Z^2 is

 , Y^3 is  , Z^3 is

 , Y^4 is  , and Z^4 is

 .

In certain instances, the present invention relates to the aforementioned method, wherein w^1 is an integer in the range of about 50 to about 250.

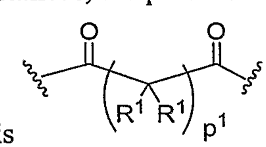
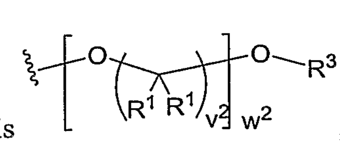
In certain instances, the present invention relates to the aforementioned method, wherein w^1 is an integer in the range of about 60 to about 90.

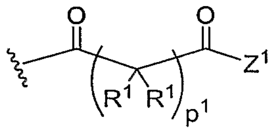
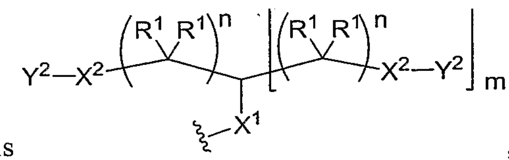
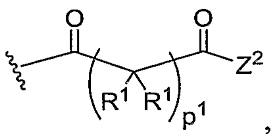
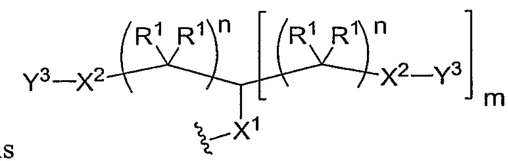
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

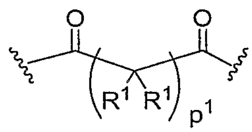
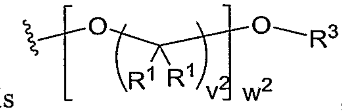
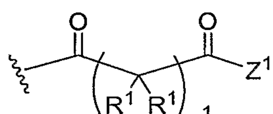
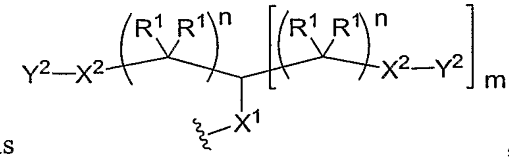
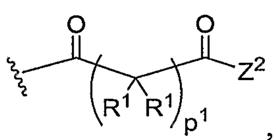
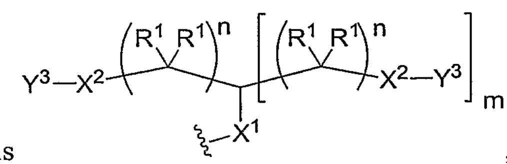
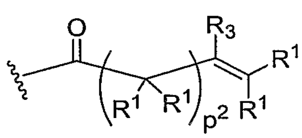
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

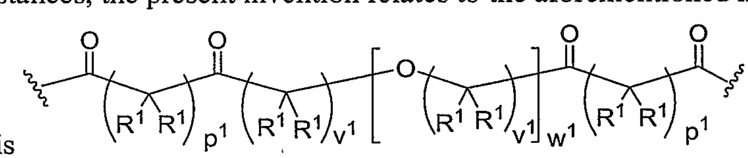
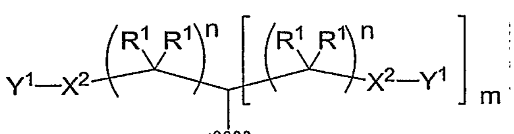
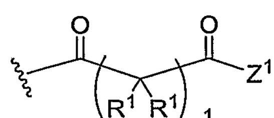
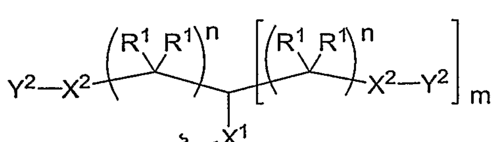
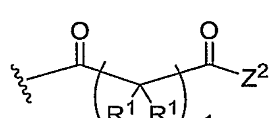
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl.

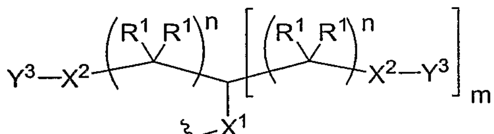
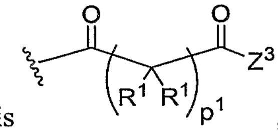
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, R^3 is $(C_1\text{-}C_5)$alkyl, and w^1 is an integer in the range of about 60 to about 90.

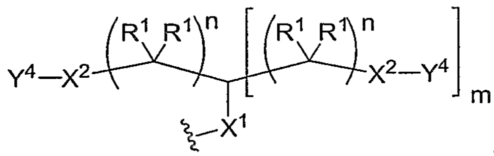
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , R^3 is alkyl, v^2 is

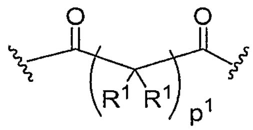
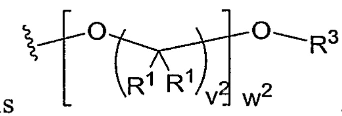
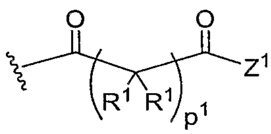
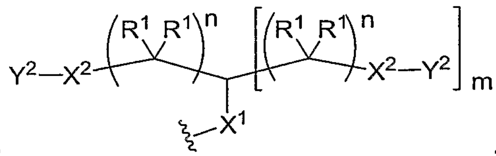
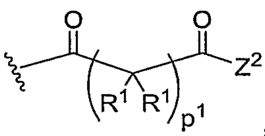
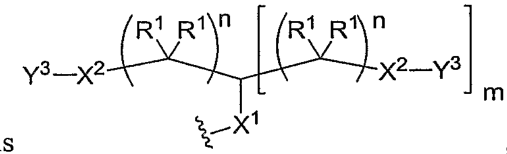
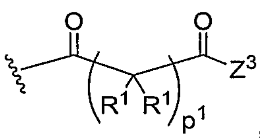
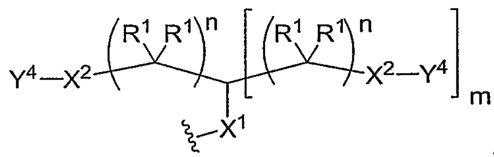
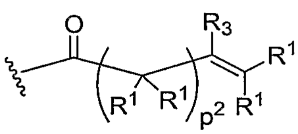
2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is .

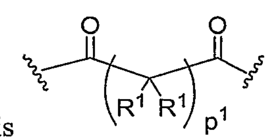
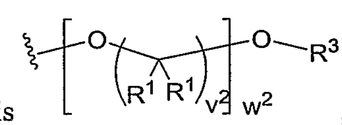
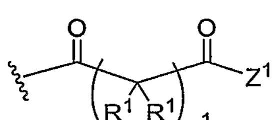
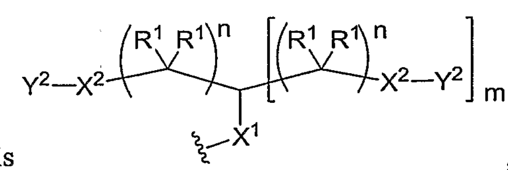
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

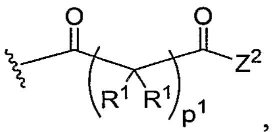
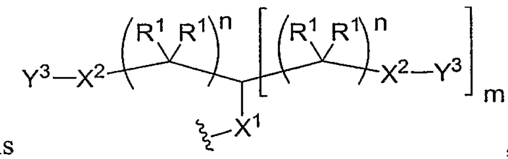
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is

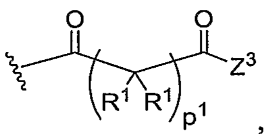
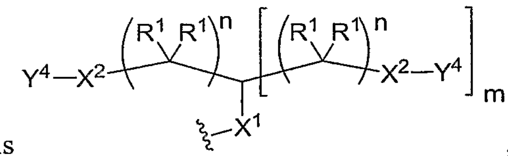
 , Y^3 is  , and Z^3 is

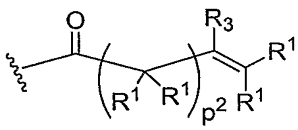
 .

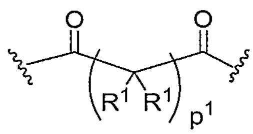
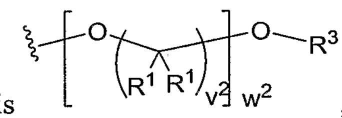
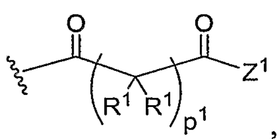
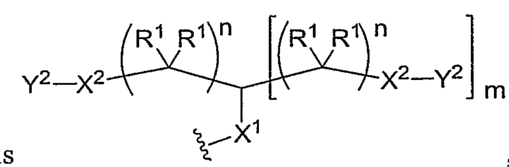
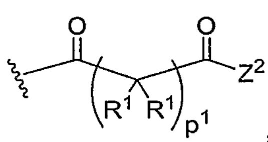
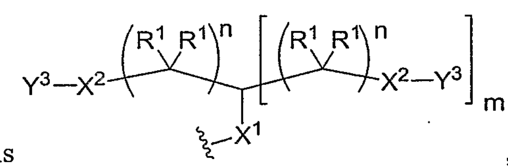
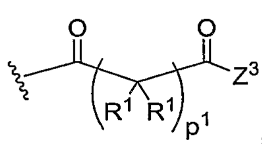
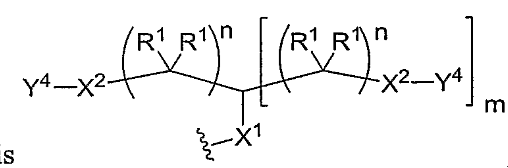
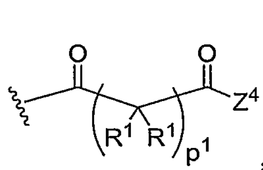
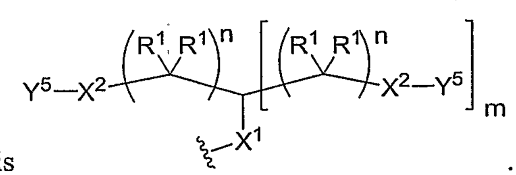
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , R^3 is alkyl, v^2 is 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , and Y^4 is  .

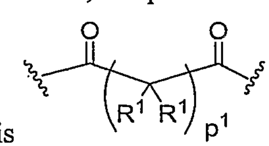
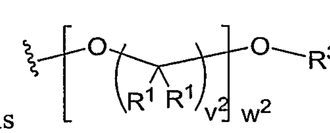
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , R^3 is alkyl, v^2 is 2, Y^1 is  , Z^1 is  , Y^2 is

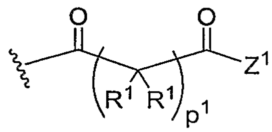
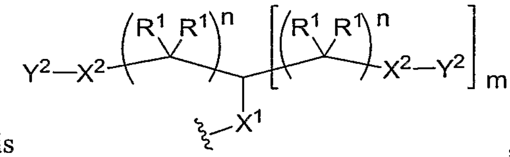
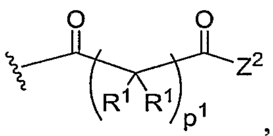
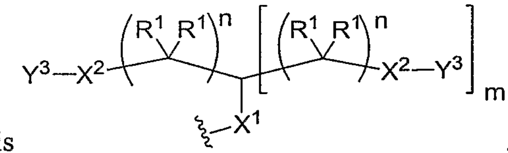
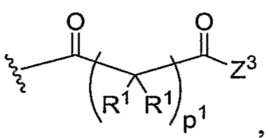
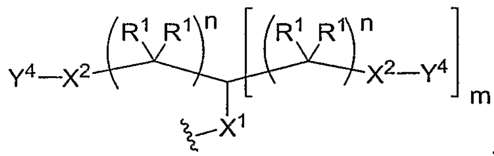
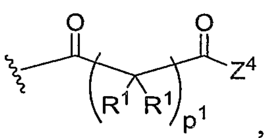
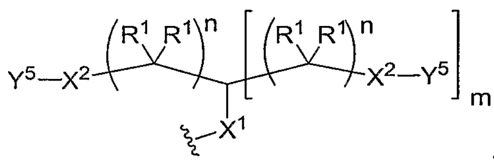
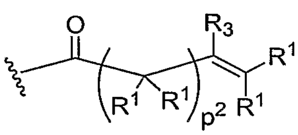
, Z^2 is , Y^3 is

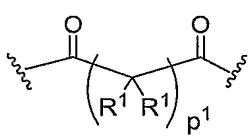
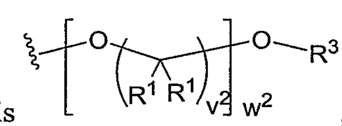
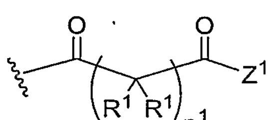
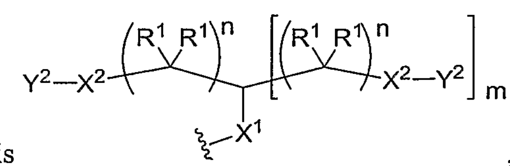
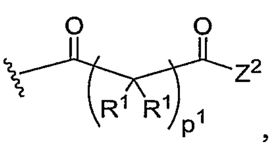
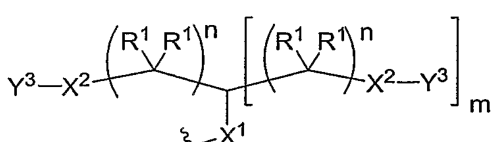
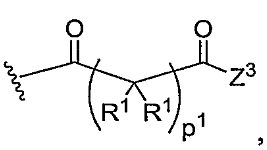
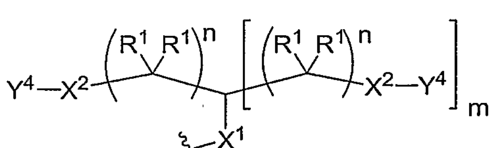
, Z^3 is , Y^4 is

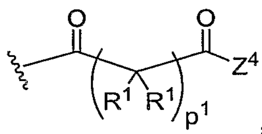
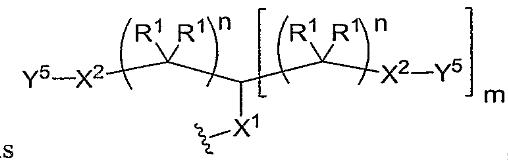
, and said polymerization agent is ultraviolet light or visible light.

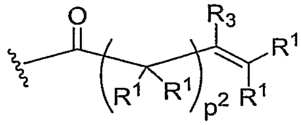
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , and Z^4 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is

2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , Z^4 is , and Y^5 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is

 , Z^4 is  , Y^5 is

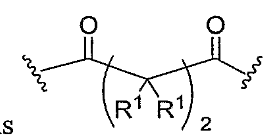
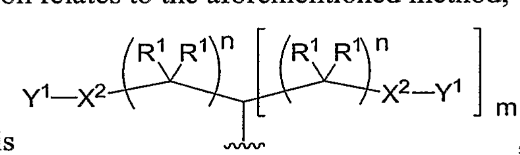
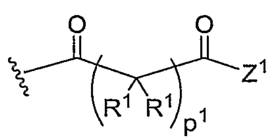
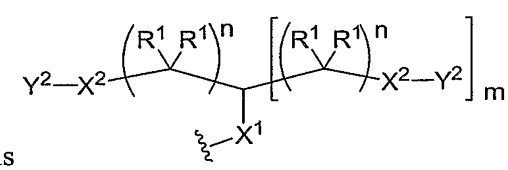
 , and said polymerization agent is ultraviolet light or visible light.

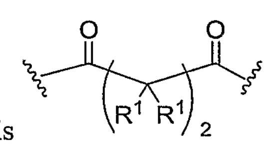
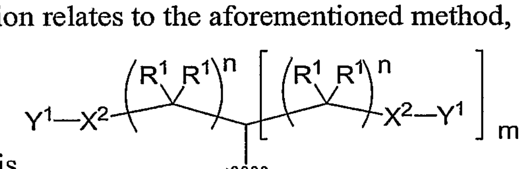
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

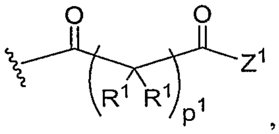
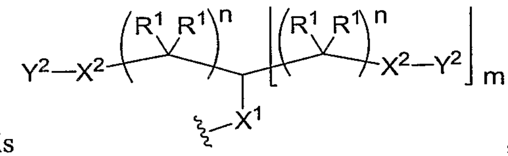
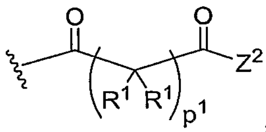
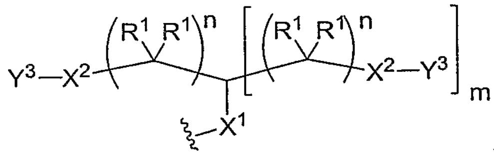
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

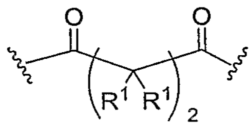
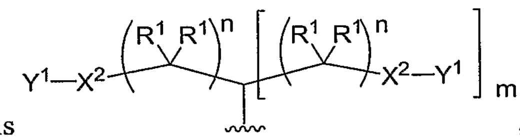
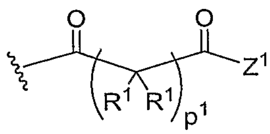
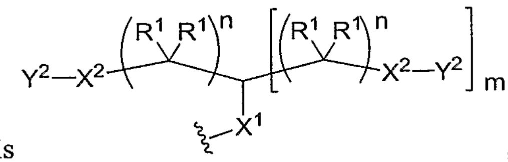
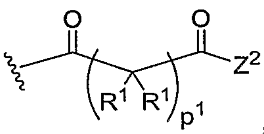
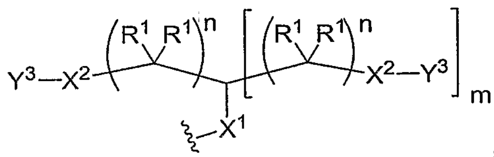
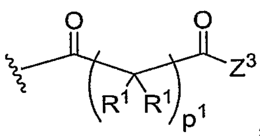
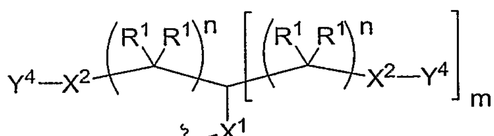
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl.

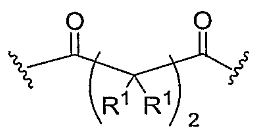
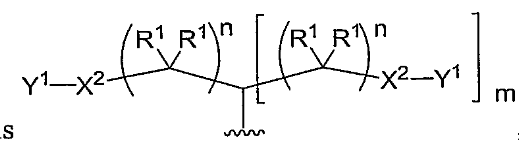
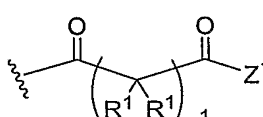
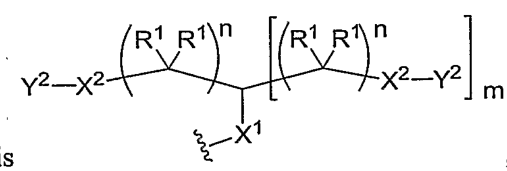
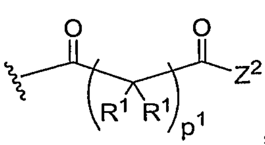
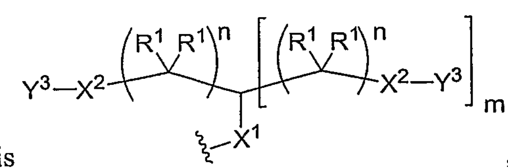
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl, and w^2 is an integer in the range of about 60 to about 90.

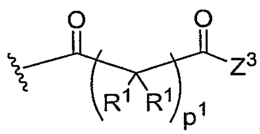
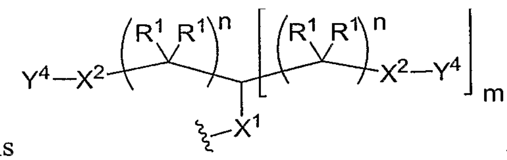
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1, or 2, Y^1 is  , and Z^1 is  .

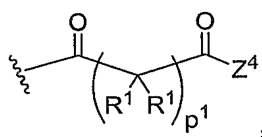
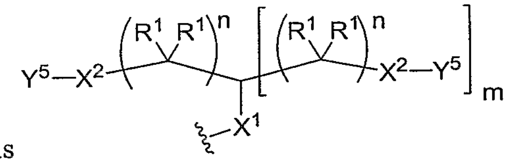
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m

is 1, or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1, or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and Z^3 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1, or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is

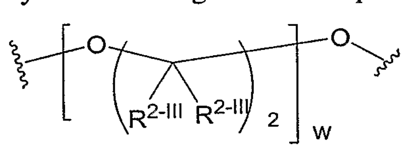
 , Z^3 is  , Y^4 is

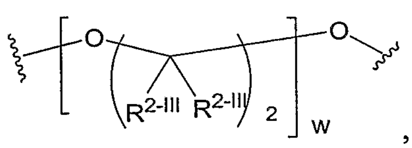
 , and Z^4 is  .

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is a compound of formula **II**.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is a compound of formula **III**.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{1\text{-}III}$ is -C(O)H, and $R^{2\text{-}III}$ is H.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{1\text{-}III}$ is -C(O)H, $R^{2\text{-}III}$ is H, and $B^{1\text{-}III}$ is  .

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{2\text{-}III}$ is -C(O)H, $R^{2\text{-}III}$ is H, $B^{1\text{-}III}$ is  , and w is an integer in the range of about 60-90.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is an oxidizing agent.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is O_2.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is ultraviolet light or visible light.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is ultraviolet light.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 400-600 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 450-550 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 488-514 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is an ophthalmic wound.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a wound to the cornea of an eye.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, corneal ulceration, retinal hole, leaking bleb, corneal transplant, trabeculectomy incision, sclerotomy incision, blepharoplasty, or skin incision.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, or corneal ulceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision or corneal laceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 25 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 15 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 10 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 5 mm long.

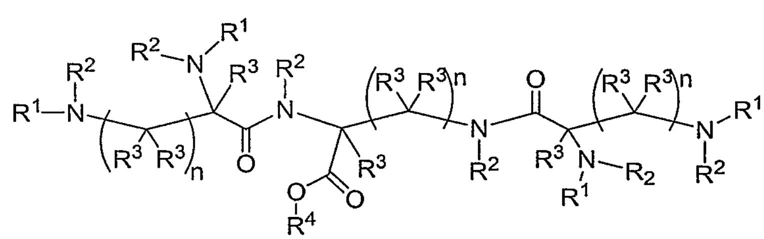
In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a method of sealing a wound of a patient, comprising the steps of:

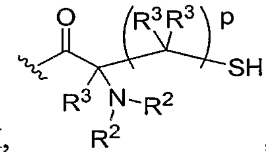
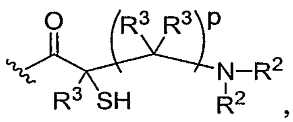
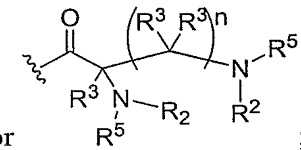
exposing a sterilized compound of formula **V** to a polymerization agent to form an adhesive composition, and applying said adhesive composition to a wound of a patient, wherein said polymerization agent is an oxidizing agent or a compound of formula **VI**, and formula **V** is represented by:



V

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

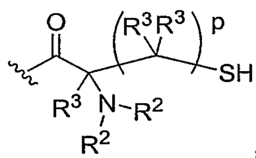
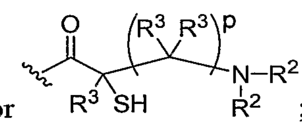
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8; and

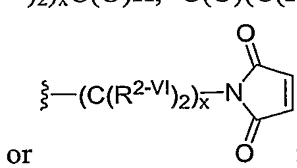
p represents independently for each occurrence 1, 2, 3, 4, or 5; and

said formula **VI** is represented by:

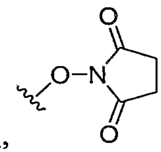
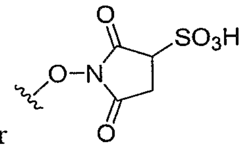
$$R^{1\text{-VI}}\text{—}B\text{—}R^{1\text{-VI}}$$

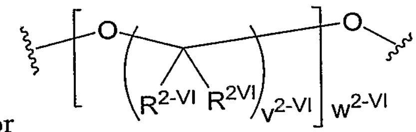
VI

wherein

$R^{1\text{-VI}}$ represents independently for each occurrence $-(C(R^{2\text{-VI}})_2)_xC(O)H$, $-C(O)(C(R^{2\text{-VI}})_2)_yC(O)H$, $-(C(R^{2\text{-VI}})_2)_xC(O)R^{3\text{-VI}}$, $-C(O)(C(R^{2\text{-VI}})_2)_yC(O)R^{3\text{-VI}}$, or ;

$R^{2\text{-VI}}$ represents independently for each occurrence H, alkyl, or halogen;

R^{3-VI} represents independently for each occurrence fluoroalkyl, chloroalkyl, -CH_2NO_2, , or ;

B is alkyl diradical, heteroalkyl diradical, or ;

v^{2-VI} represents independently for each occurrence 2, 3, or 4;

w^{2-VI} is an integer in the range of about 5 to 1000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is an oxidizing agent.

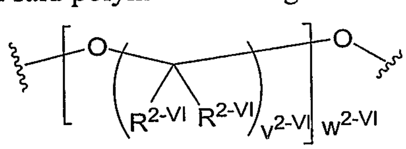
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is O_2.

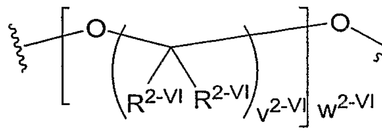
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**.

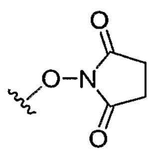
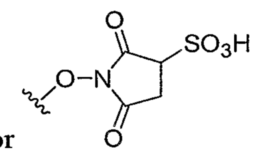
In certain instances, the present invention relates to the aforementioned method, wherein w^{2-VI} is an integer in the range of about 50 to about 250.

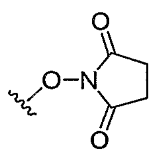
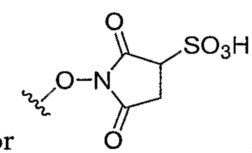
In certain instances, the present invention relates to the aforementioned method, wherein w^{2-VI} is an integer in the range of about 60 to about 90.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, R^{1-VI} is -C(O)H, and R^{2-VI} is H.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, R^{1-VI} is -C(O)H, R^{2-VI} is H, B is , and v^{2-VI} is 2.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, $R^{2\text{-}VI}$ is H, B is , $v^{2\text{-}VI}$ is 2, and $w^{2\text{-}VI}$ is an integer in the range of about 60-90.

In certain instances, the present invention relates to the aforementioned method, wherein $R^{1\text{-}VI}$ is $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$ or $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, $R^{2\text{-}VI}$ is H, and $R^{3\text{-}VI}$ is  or .

In certain instances, the present invention relates to the aforementioned method, wherein $R^{1\text{-}VI}$ is $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$ or $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, $R^{2\text{-}VI}$ is H, $R^{3\text{-}VI}$ is  or , $v^{2\text{-}VI}$ is 2, and $w^{2\text{-}VI}$ is an integer in the range of about 15-90.

In certain instances, the present invention relates to the aforementioned method, wherein n is 3, 4, or 5.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4.

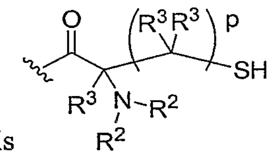
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is H.

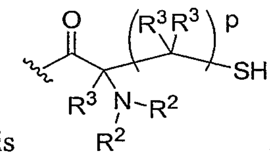
In certain instances, the present invention relates to the aforementioned method, wherein R^3 is H.

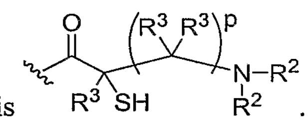
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is alkyl.

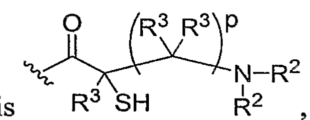
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is methyl or ethyl.

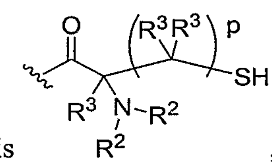
In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

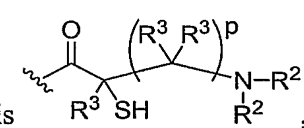
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and a Bronstead acid.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of

formula **V** and HA, wherein A is halogen or $-O_2CR^o$, and R^o is alkyl, fluoroalkyl, aryl, or aralkyl.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and an acid selected from group consisting of HCl and HBr.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and HO_2CR^6, wherein R^6 is fluoroalkyl.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and CF_3CO_2H.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is an ophthalmic wound.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a wound to the cornea of an eye.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, corneal ulceration, retinal hole, leaking bleb, corneal transplant, trabeculectomy incision, sclerotomy incision, blepharoplasty, or skin incision.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, or corneal ulceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision or corneal laceration

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 25 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 15 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 10 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 5 mm long.

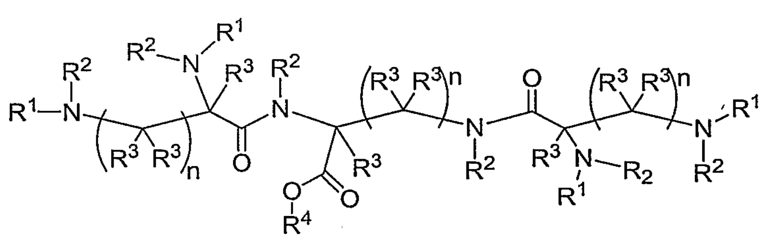
In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said compound of formula **V** and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, wherein said compound of formula **V** and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a method of sealing a wound of a patient, comprising the steps of:

exposing a dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X** to a polymerization agent to form an adhesive composition, and applying said adhesive composition to a wound of a patient, wherein said polymerization agent is an oxidizing agent or a compound of formula **XI**, and wherein formula **VII** is represented by:

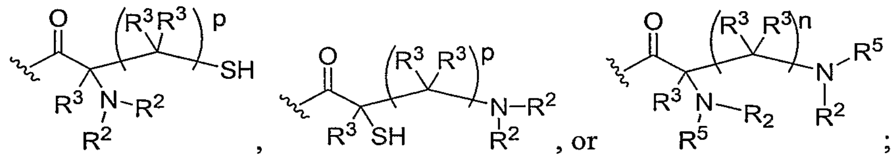


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

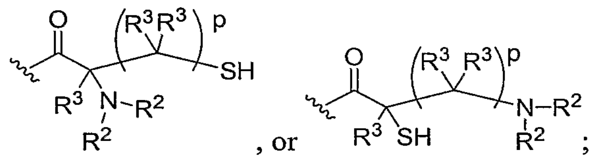


R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

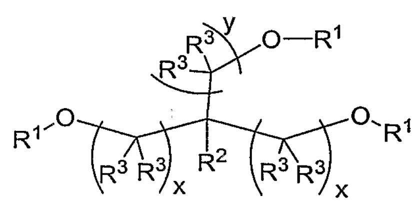
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,



n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

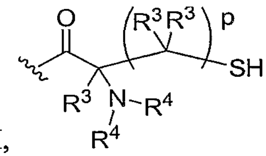
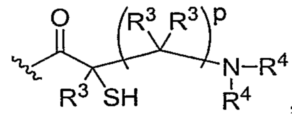
formula **VIII** is represented by:

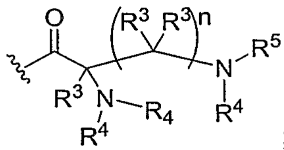


VIII

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$, , , or

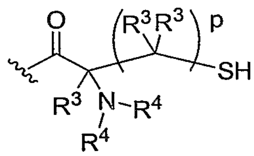
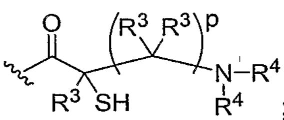
;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

, or ;

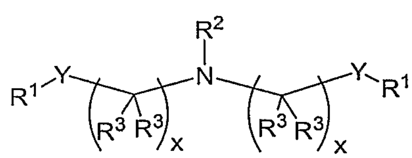
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

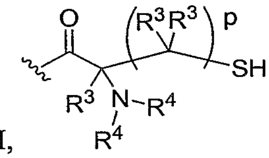
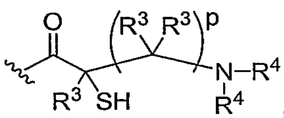
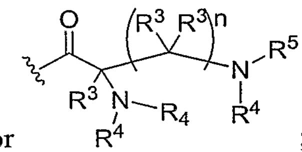
y is 0, 1, 2, 3, or 4;

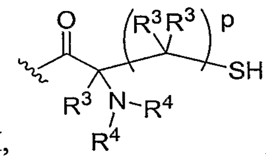
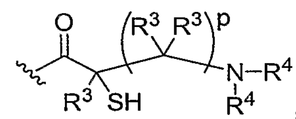
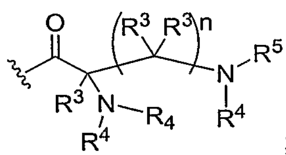
formula **IX** is represented by:



IX

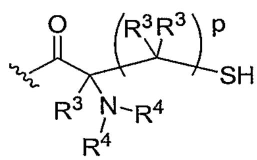
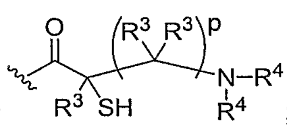
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

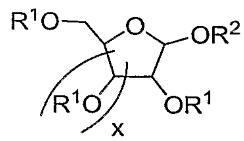
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

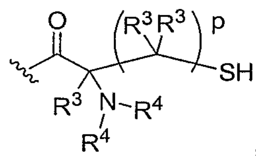
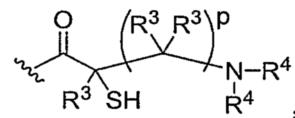
x represents independently for each occurrence 1, 2, 3, or 4;

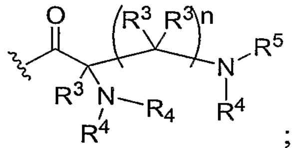
formula **X** is represented by:



X

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or

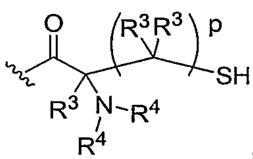
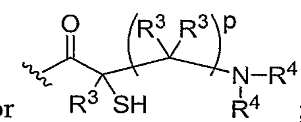
 ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2; and

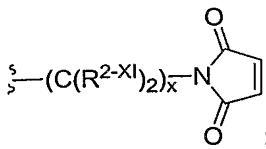
formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

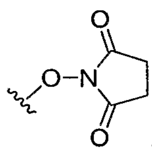
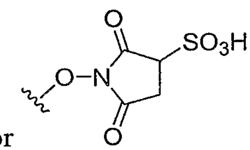
XI

wherein

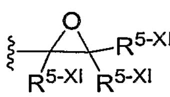
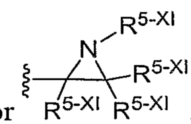
R^{1-XI} represents independently for each occurrence $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$, $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, $-(C(R^{2-XI})_2)_xR^{4-XI}$, $-C(O)(C(R^{2-XI})_2)_yR^{4-XI}$, or


;

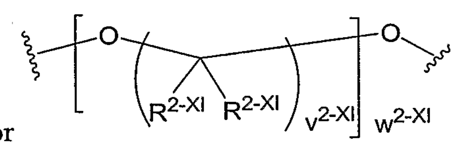
R^{2-XI} represents independently for each occurrence H, alkyl, or halogen;

R^{3-XI} represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

R^{4-XI} represents independently for each occurrence -N=C=O, -N=C=S,

 , or  ;

R^{5-XI} represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or  ;

v^{2-XI} represents independently for each occurrence 2, 3, or 4;

w^{2-XI} is an integer in the range of about 5 to 1000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

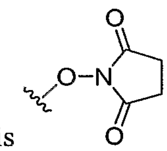
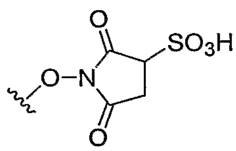
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is an oxidizing agent.

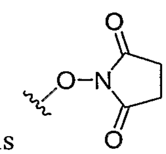
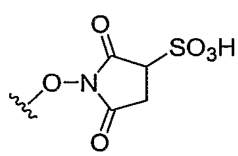
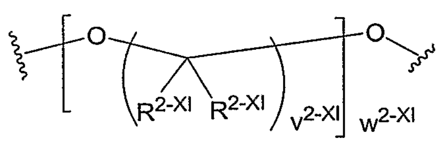
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is O_2.

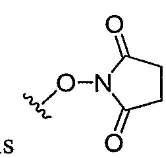
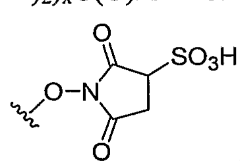
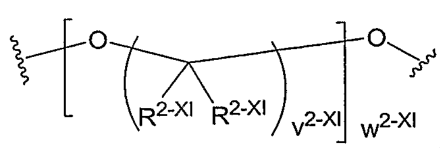
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**.

In certain instances, the present invention relates to the aforementioned method, wherein $w^{2\text{-}XI}$ is an integer in the range of about 50 to about 250.

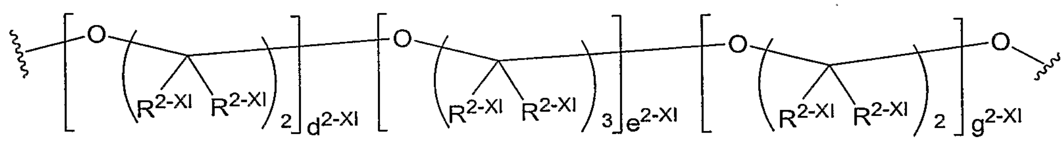
In certain instances, the present invention relates to the aforementioned method, wherein $w^{2\text{-}XI}$ is an integer in the range of about 60 to about 90.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is  or .

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is  or , B is , and $v^{2\text{-}XI}$ is 2.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is  or , B is , $v^{2\text{-}VII}$ is 2, and $w^{2\text{-}XI}$ is an integer in the range of about 15-90.

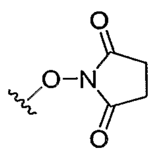
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, wherein B is



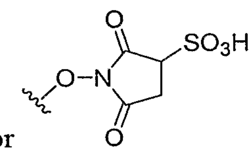
, and

$d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ represent independently an integer greater than zero, provided that the sum of $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ is an integer in the range of about 5 to 500, inclusive.

In certain instances, the present invention relates to the aforementioned method, wherein, $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is

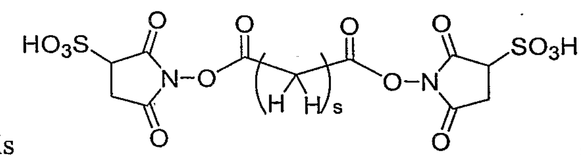


or



.

In certain instances, the present invention relates to the aforementioned method, wherein, formula **XI** is



, and s is an integer in the range of about 1-20, inclusive.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VII**.

In certain instances, the present invention relates to the aforementioned method, wherein n is 3, 4, or 5.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4.

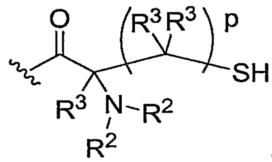
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is H.

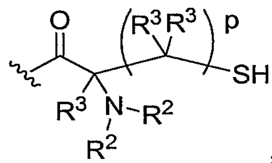
In certain instances, the present invention relates to the aforementioned method, wherein R^3 is H.

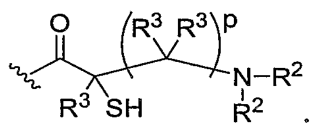
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is alkyl.

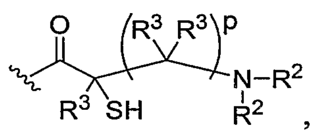
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is methyl or ethyl.

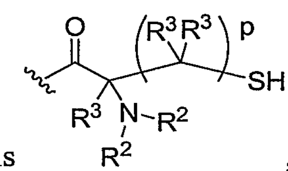
In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

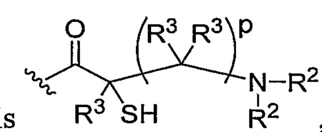
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**, x and y are 1, R^2 is -CH_2OR^1, and R^3 is H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**, x is 1, y is 0, and R^2 and R^3 are H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is O, R^2 is -$CH_2CH_2OR^1$, and R^3 is H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is NR^4, and R^2 and R^3 are H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **X**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **X**, R^2 is methyl, and x is 2.

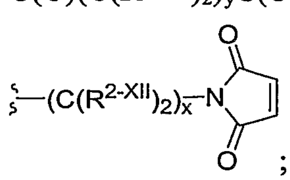
In certain instances, the present invention relates to the aforementioned method, further comprising the step of exposing said dendrimeric compound to a compound of formula **XII**, wherein formula **XII** is represented by:

$$R^{1\text{-}XII}—B^{XII}—R^{1\text{-}XII}$$

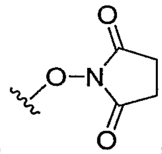
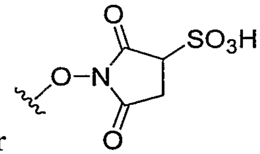
XII

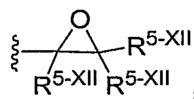
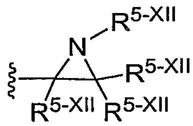
wherein

$R^{1\text{-}XII}$ represents independently for each occurrence -$(C(R^{2\text{-}XII})_2)_xC(O)R^{3\text{-}XII}$, -$C(O)(C(R^{2\text{-}XII})_2)_yC(O)R^{3\text{-}XII}$, -$(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XII}$, -$C(O)(C(R^{2\text{-}XII})_2)_yR^{4\text{-}XII}$, or

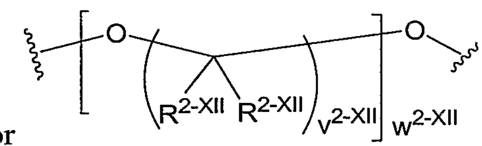

;

R^{2-XII} represents independently for each occurrence H, alkyl, or halogen;

R^{3-XII} represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2, , or  ;

R^{4-XI} represents independently for each occurrence -N=C=O, -N=C=S, , or  ;

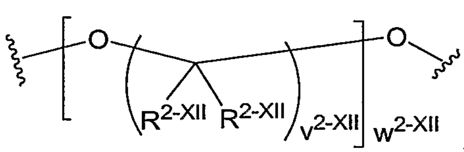
R^{5-XI} represents independently for each occurrence H, alkyl, or aralkyl;

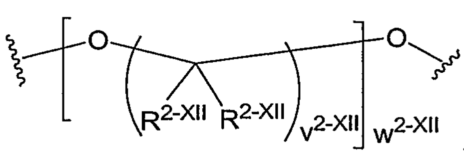
B^{XII} is alkyl diradical, heteroalkyl diradical, or  ;

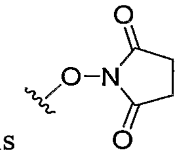
v^{2-XII} represents independently for each occurrence 2, 3, or 4;

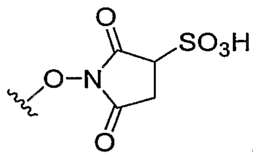
w^{2-XII} is an integer in the range of about 5 to 1000, inclusive; and

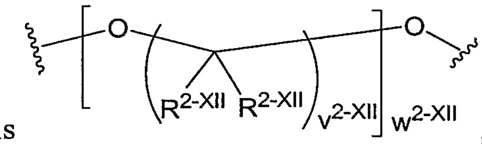
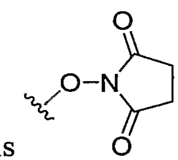
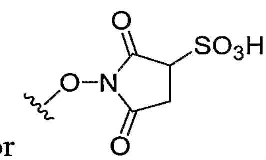
x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

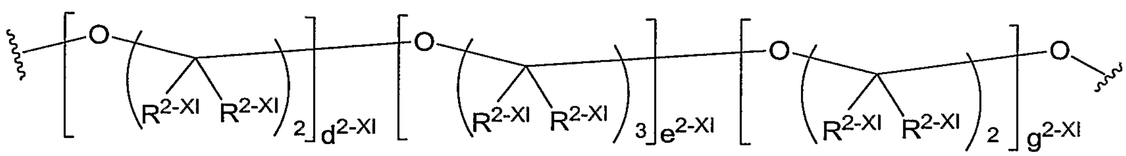
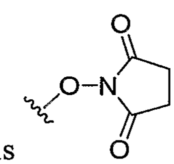
In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is  , and v^{2-XII} is 2.

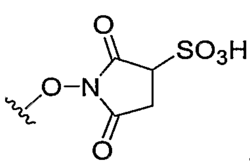
In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is  , v^{2-XII} is 2, R^{1-XII} is -$(C(R^{2-XII})_2)_xC(O)R^{3-}$

XII or -C(O)(C($R^{2\text{-}XII}$)$_2$)$_y$C(O)$R^{3\text{-}XII}$, $R^{2\text{-}XII}$ is H, and $R^{3\text{-}XII}$ is  or

 .

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is  , $v^{2\text{-}XII}$ is 2, $R^{1\text{-}XII}$ is -(C($R^{2\text{-}XII}$)$_2$)$_x$C(O)$R^{3\text{-}XII}$ or -C(O)(C($R^{2\text{-}XII}$)$_2$)$_y$C(O)$R^{3\text{-}XII}$, $R^{2\text{-}XII}$ is H, $R^{3\text{-}XII}$ is  or  , said polymerization agent is a compound of formula **XI**, B is

 , $R^{1\text{-}XI}$ is -(C($R^{2\text{-}XI}$)$_2$)$_x$C(O)$R^{3\text{-}XI}$ or -C(O)(C($R^{2\text{-}XI}$)$_2$)$_y$C(O)$R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or

 , and $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ represent independently an integer greater than zero, provided that the sum of $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ is an integer in the range of about 5 to 1000, inclusive.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is an ophthalmic wound.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a wound to the cornea of an eye.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, corneal ulceration, retinal hole, leaking bleb, corneal transplant, trabeculectomy incision, sclerotomy incision, blepharoplasty, or skin incision.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision, corneal laceration, corneal perforation, or corneal ulceration.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is a corneal incision or corneal laceration

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 25 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 15 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 10 mm long.

In certain embodiments, the present invention relates to the aforemention method, wherein said wound is less than 5 mm long.

In certain embodiments, the present invention relates to the aforemention method, further comprising the step of sterilizing said polymerization agent.

In certain embodiments, the present invention relates to the aforemention method, wherein said sterilizing is performed by treatment with ethylene oxide, hydrogen peroxide, heat, gamma irradiation, electron beam irradiation, microwave irradiation, or visible light irradiation.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

Methods of the Invention Relating to Preparing a Lens

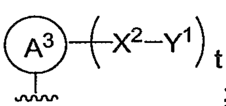
Another aspect of the present invention relates to a method of preparing an ocular lens for a patient, comprising the steps of:

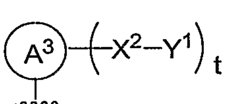
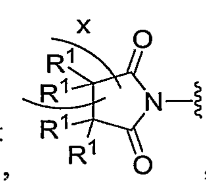
exposing a sterilized dendrimeric compound of formula **I** to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is ultraviolet light, visible light, a compound of formula **II**, a compound of formula **III**, a compound of formula **IV**, or an oxidizing agent, wherein formula **I** is represented by:

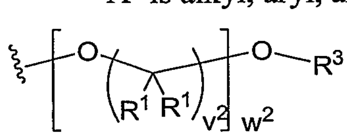
$$A^1—X^1—B—X^1—A^2$$

I

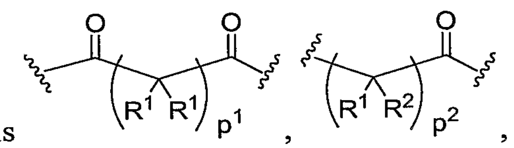
wherein

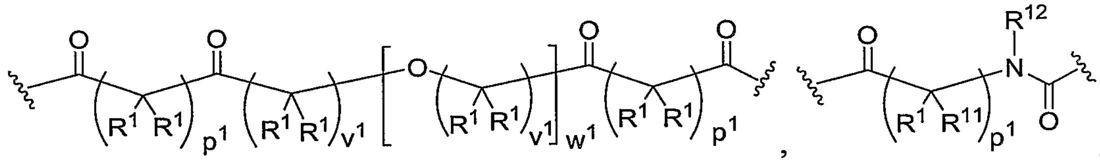
A^1 is  ;

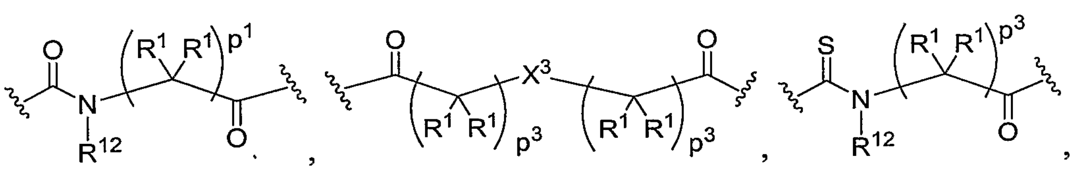
A^2 is alkyl, aryl, aralkyl, -Si(R^3)$_3$,  ,  , or

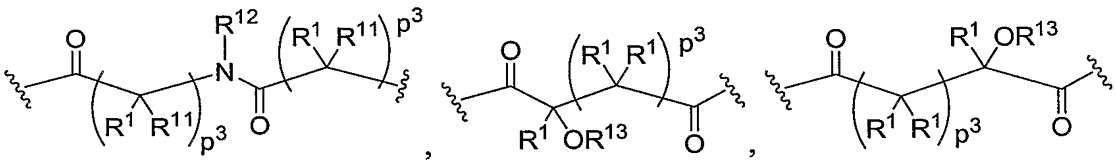
 ;

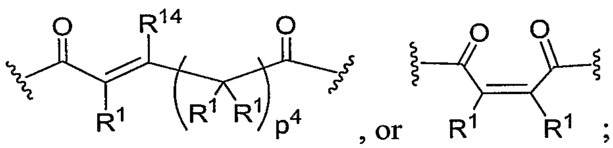
A^3 represents independently for each occurrence alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, heteroaryl, or aralkyl;

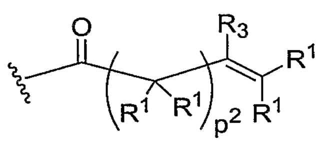
B is 

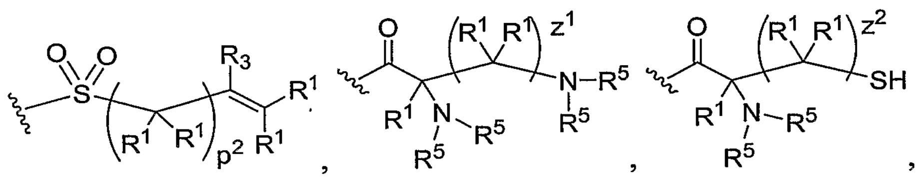


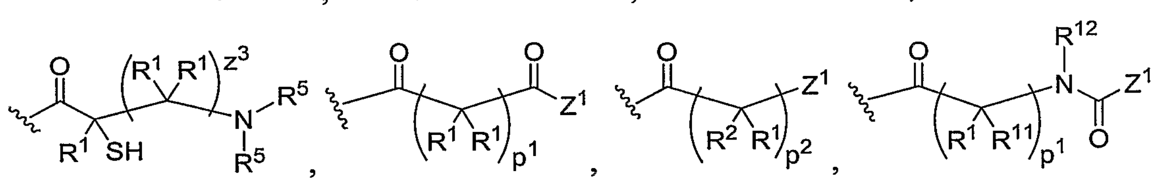


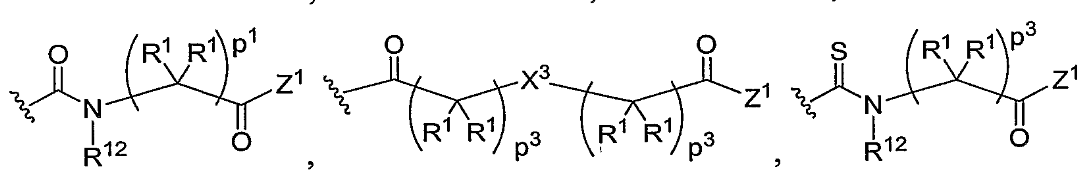


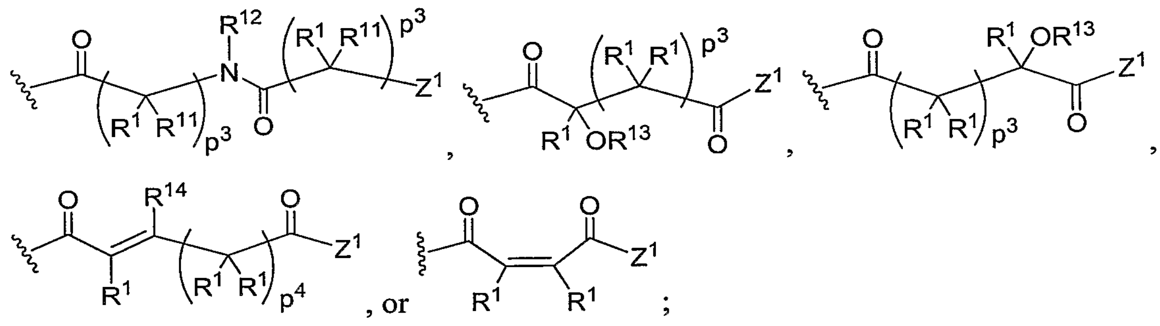
 ;

Y^1 represents independently for each occurrence R^4, A^4, 

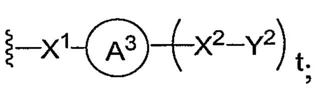


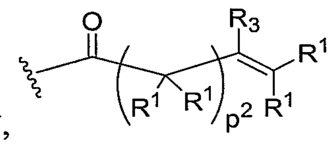


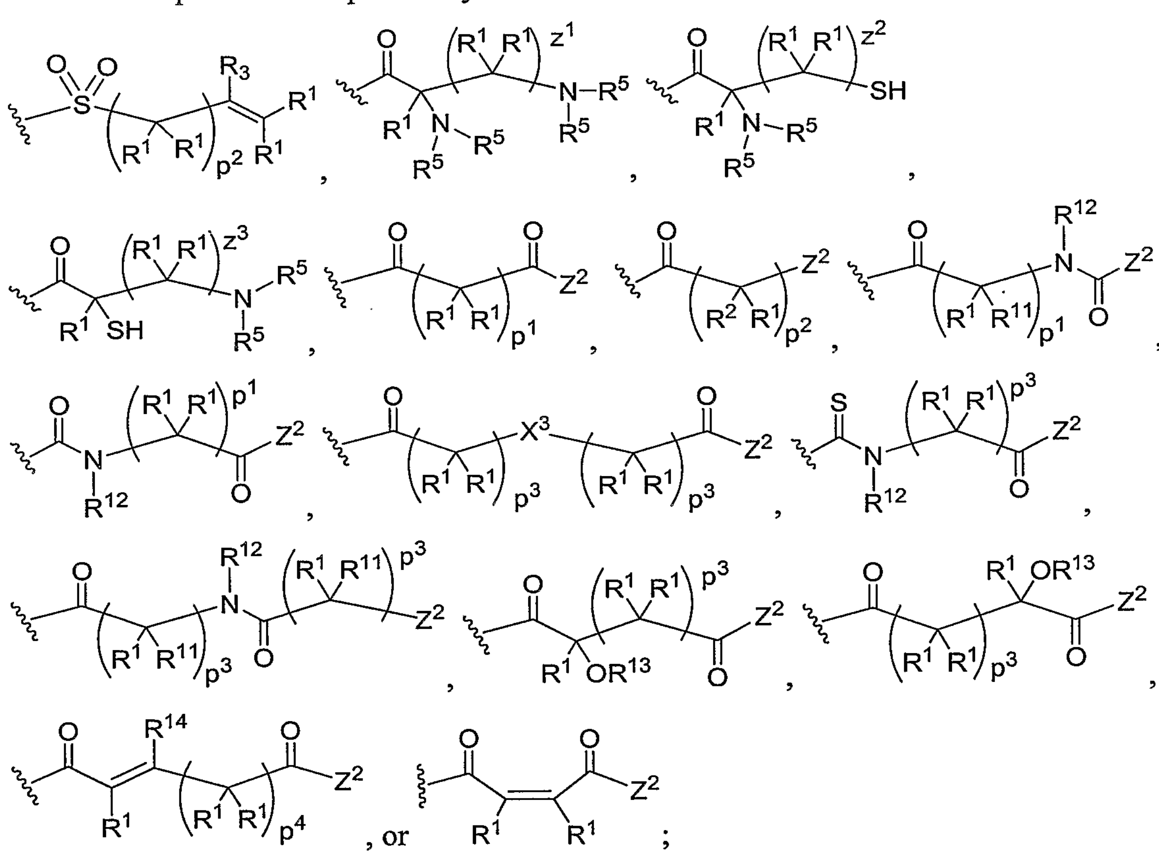




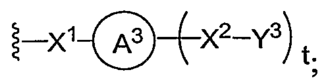
Z^1 represents independently for each occurrence $-X^1-R^4$, E, or

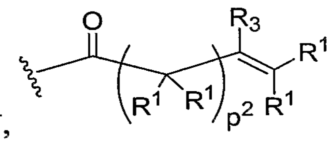


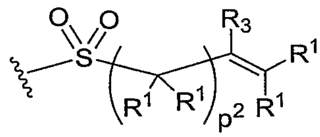
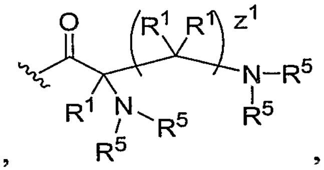
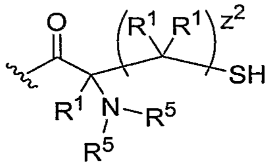
Y^2 represents independently for each occurrence R^5, A^4, 

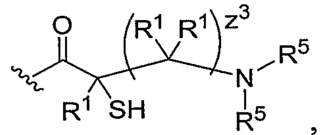
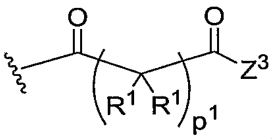
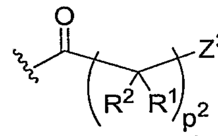
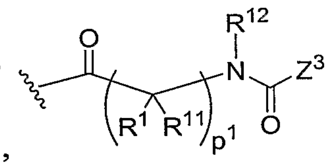


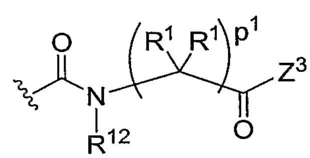
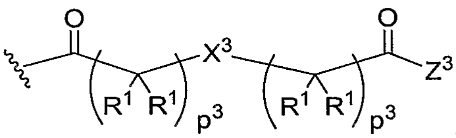
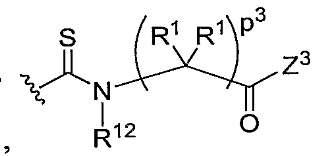
Z^2 represents independently for each occurrence $-X^1-R^5$, E, or

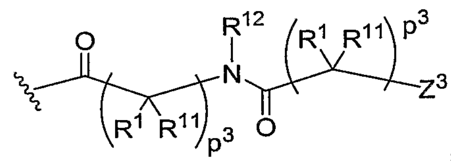
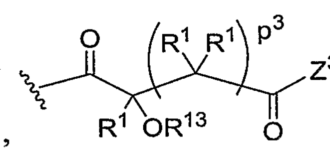
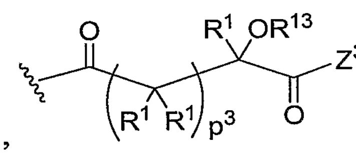


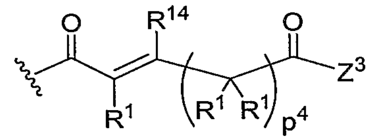
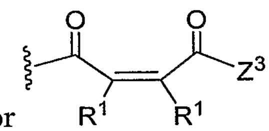
Y^3 represents independently for each occurrence R^6, A^4, ,

, , ,

, , , ,

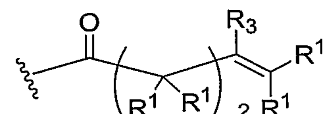
, , ,

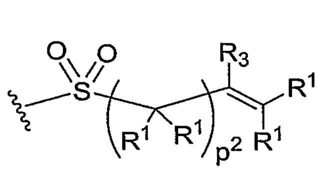
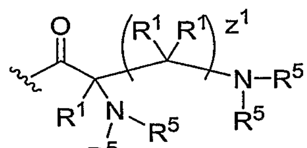
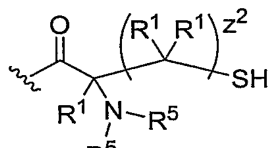
, , ,

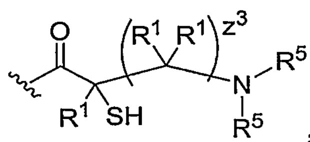
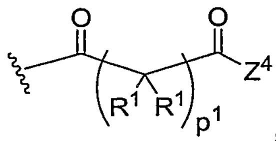
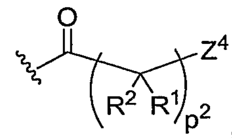
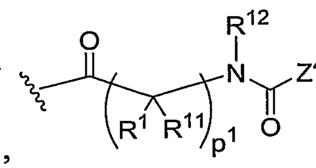
, or ;

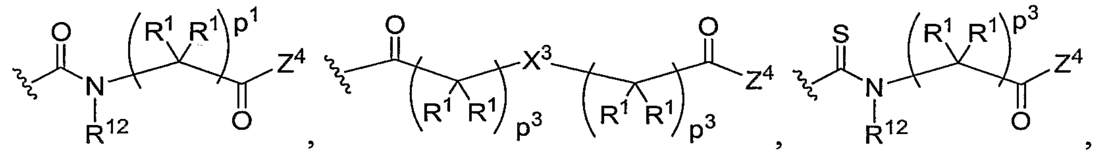
Z^3 represents independently for each occurrence $-X^1-R^6$, E, or

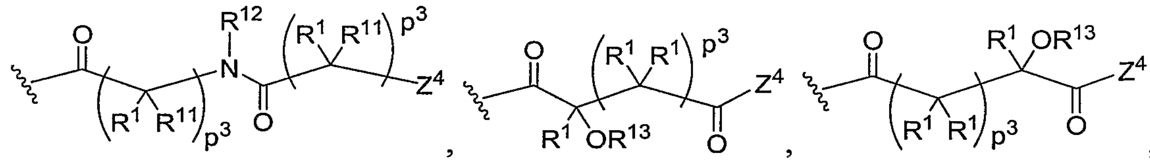
$-X^1-A^3-(X^2-Y^4)_t$;

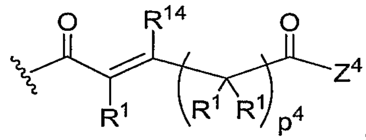
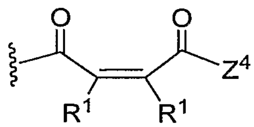
Y^4 represents independently for each occurrence R^7, A^4, ,

, , ,

, , , ,

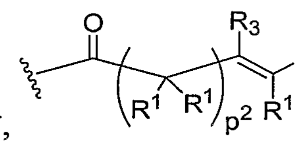


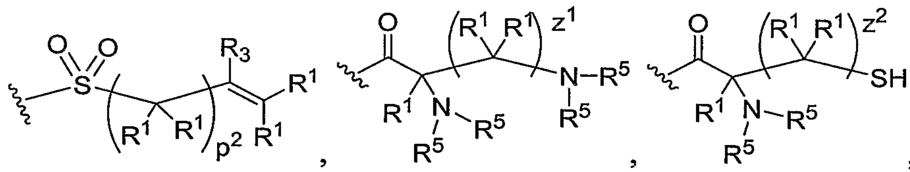


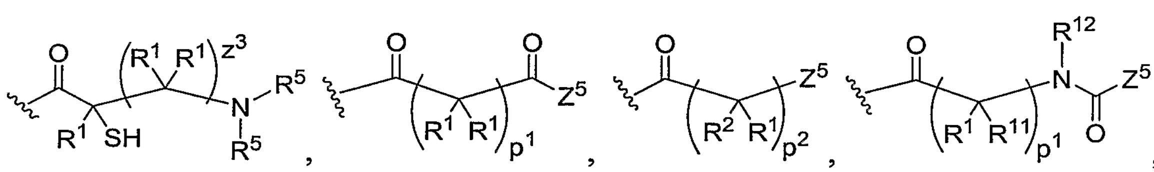
 , or  ;

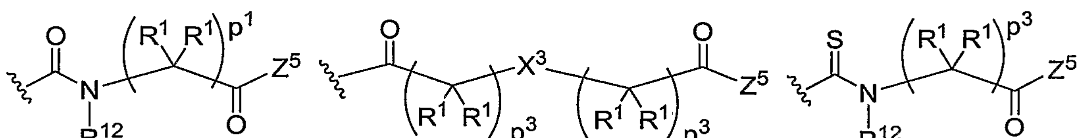
Z^4 represents independently for each occurrence $-X^1-R^7$, E, or

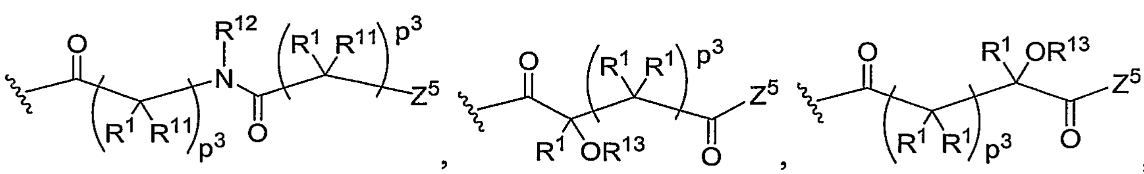
$\text{⌇}-X^1-(A^3)-(X^2-Y^5)_t$;

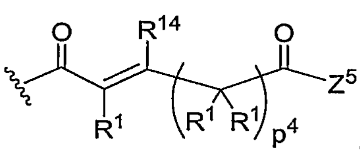
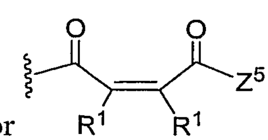
Y^5 represents independently for each occurrence R^8, A^4,  ,



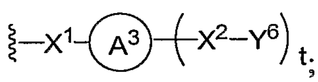


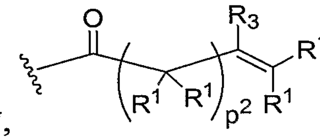


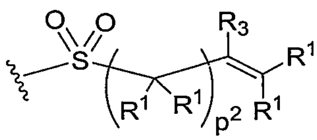
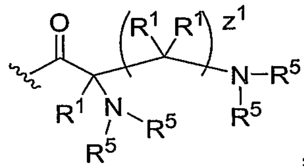
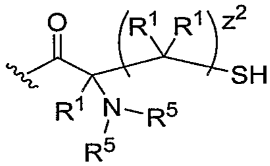


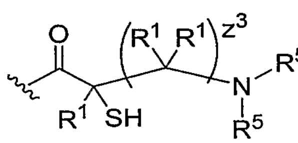
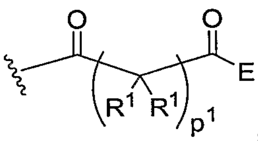
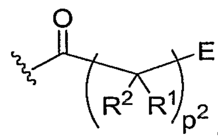
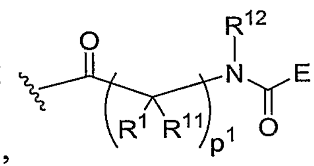
 , or  ;

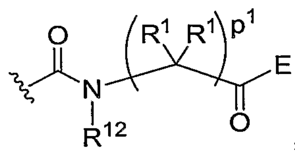
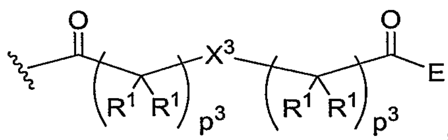
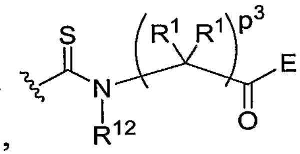
Z^5 represents independently for each occurrence $-X^1-R^8$, E, or

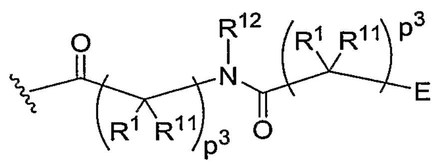
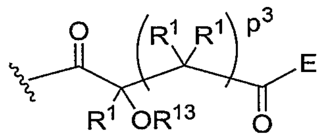
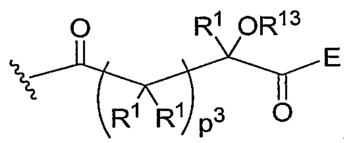
;

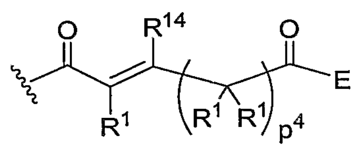
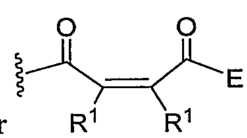
Y^6 represents independently for each occurrence R^9, A^4, ,

, , ,

, , , ,

, , ,

, , ,

, or ;

R^1 represents independently for each occurrence H, alkyl, or halogen;

R^2 represents independently for each occurrence H, alkyl, -OH, -N(R^{10})$_2$, -SH, hydroxyalkyl, or -[C(R^1)$_2$]$_d$R^{16};

R^3 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^4, R^5, R^6, R^7, R^8, and R^9 are H;

R^{10} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{11} represents independently for each occurrence H, -OH, -N(R^{10})$_2$, -SH, alkyl, hydroxyalkyl, or -[C(R^1)$_2$]$_d$R^{16};

R^{12} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{13} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{14} represents independently for each occurrence H, alkyl, or $-CO_2R^{10}$;

R^{15} represents independently for each occurrence H, alkyl, or $-OR^{10}$;

R^{16} represents independently for each occurrence phenyl, hydroxyphenyl, pyrrolidyl, imidazolyl, indolyl, $-N(R^{10})_2$, -SH, -S-alkyl, $-CO_2R^{10}$, $-C(O)N(R^{10})_2$, or $-C(NH_2)N(R^{10})_2$;

d represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

n represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

p^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7; or 8;

p^2 represents independently for each occurrence 0, 1, 2, 3, or 4;

p^3 represents independently for each occurrence 1, 2, or 3;

p^4 represents independently for each occurrence 0, 1, 2, or 3;

t represents independently for each occurrence 2, 3, 4, or 5 in accord with the rules of valence;

v^1 and v^2 each represent independently for each occurrence 2, 3, or 4;

w^1 and w^2 each represent independently for each occurrence an integer from about 5 to about 700, inclusive;

x is 1, 2, or 3;

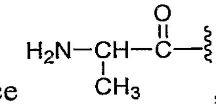
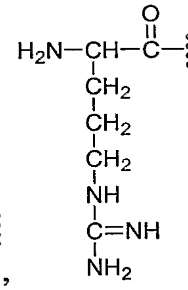
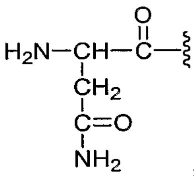
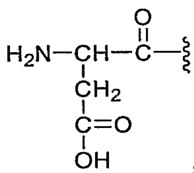
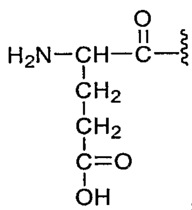
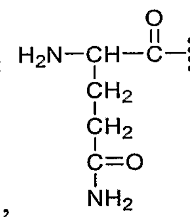
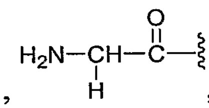
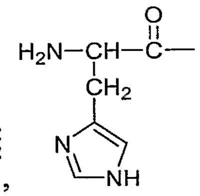
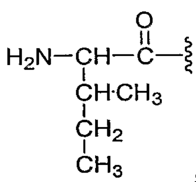
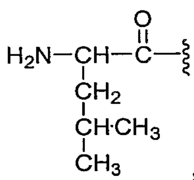
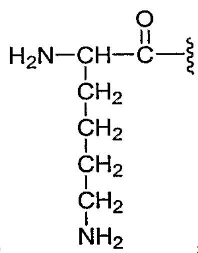
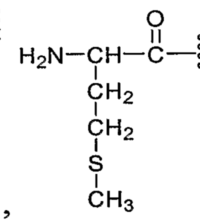
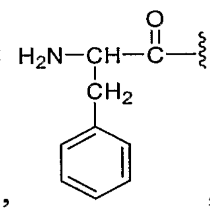
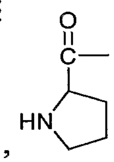
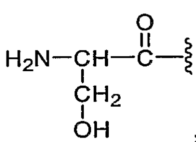
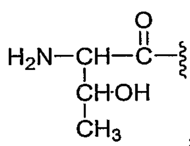
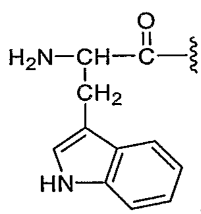
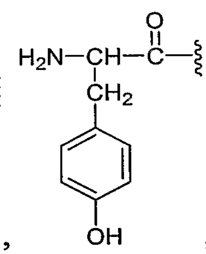
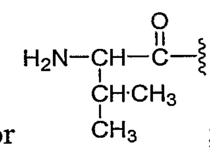
y is 0, 1, 2, 3, 4, or 5;

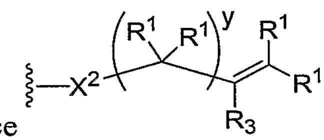
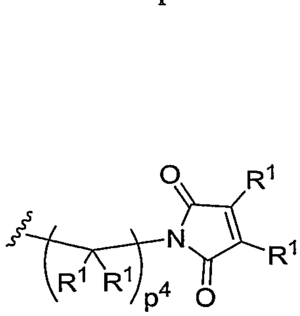
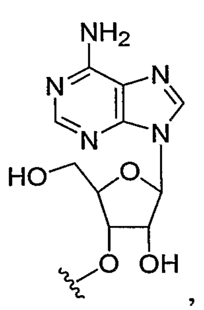
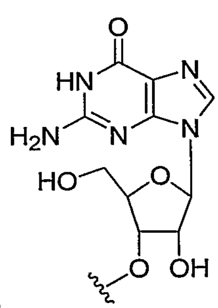
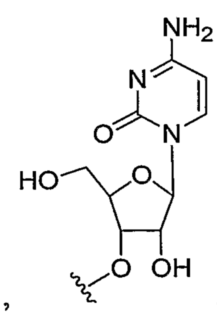
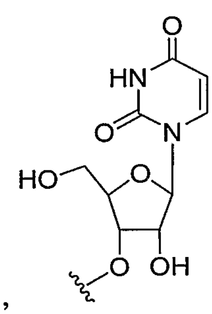
z^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

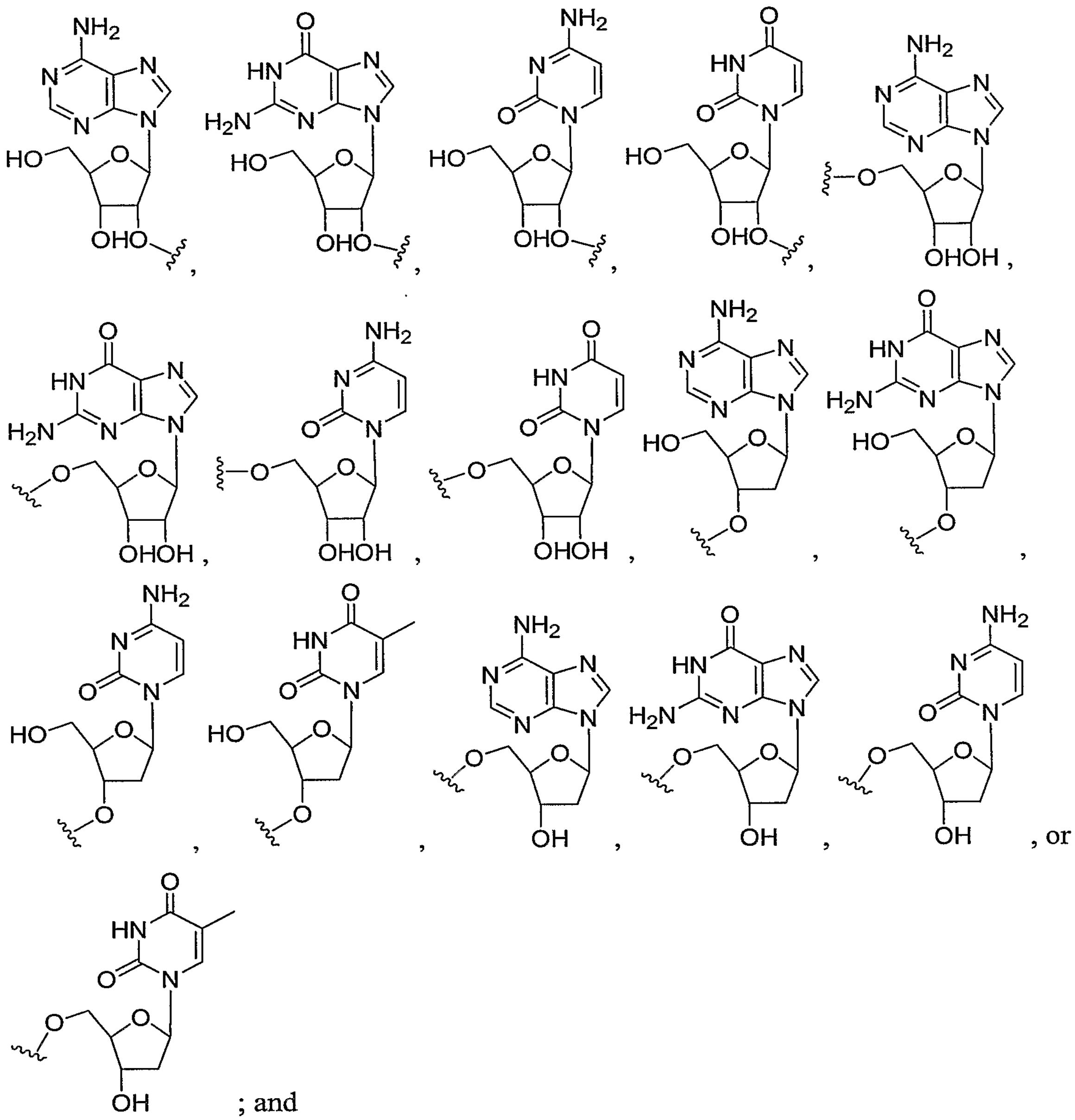
z^2 and z^3 each represent independently for each occurrence 1, 2, 3, 4, or 5;

X^1 and X^2 each represent independently for each occurrence O or $-N(R^{10})-$;

X^3 represents independently for each occurrence O, $N(R^{10})$, or $C(R^{15})(CO_2R^{10})$;

A^4 represents independently for each occurrence , , , , , , , , , , , , , , , , , , or ;

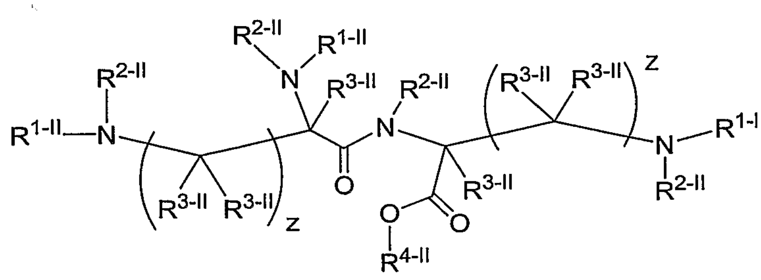
E represents independently for each occurrence , , , , , ,



; and

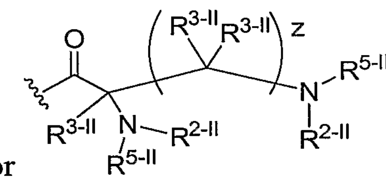
provided that R^4 only occurs once, R^5 only occurs once, R^6 only occurs once, R^7 only occurs once, R^8 only occurs once, and R^9 only occurs once;

said formula **II** is represented by:



II

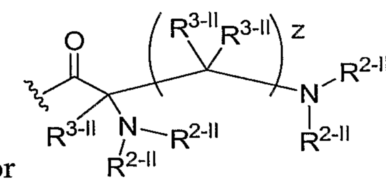
wherein

$R^{1\text{-}II}$ represents independently for each occurrence H or  ;

$R^{2\text{-}II}$ represents independently for each occurrence H or alkyl;

$R^{3\text{-}II}$ represents independently for each occurrence H, halogen, or alkyl;

$R^{4\text{-}II}$ represents independently for each occurrence alkyl, aryl, or aralkyl;

$R^{5\text{-}II}$ represents independently for each occurrence H or  ;

and

z represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8; and

said formula **III** is represented by:

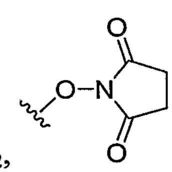
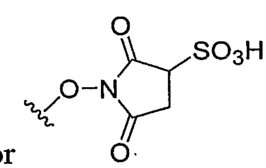
$$R^{1\text{-}III}—B^{1\text{-}III}—R^{1\text{-}III}$$

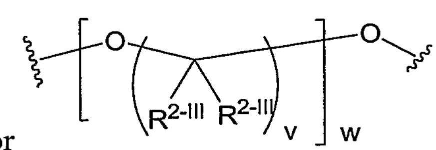
III

wherein

$R^{1\text{-}III}$ is $-(C(R^{2\text{-}III})_2)_xC(O)H$, $-C(O)(C(R^{2\text{-}III})_2)_yC(O)H$, $-(C(R^{2\text{-}III})_2)_xC(O)R^{3\text{-}III}$, or $-C(O)(C(R^{2\text{-}III})_2)_yC(O)R^{3\text{-}III}$;

$R^{2\text{-}III}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}III}$ is fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

$B^{1\text{-}III}$ is alkyl diradical, heteroalkyl diradical, or  ;

x represents independently for each occurrence 0, 1, 2, 3, 4, 5, 6, 7, or 8;

y represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

v represents independently for each occurrence 2, 3, or 4; and

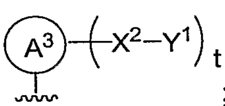
w is an integer in the range of about 5 to about 7000, inclusive; and

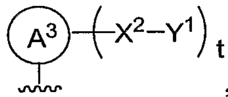
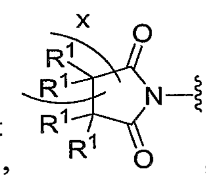
wherein formula **IV** is represented by:

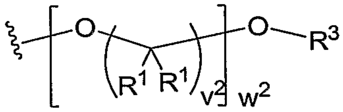
$$A^1—X^1—B—X^1—A^2$$

IV

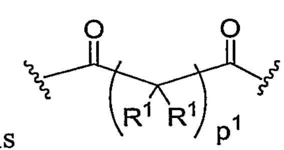
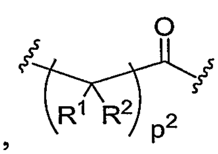
wherein

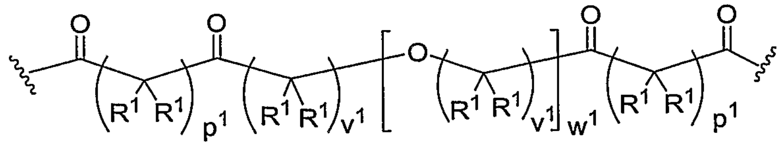
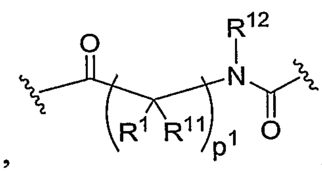
A^1 is  ;

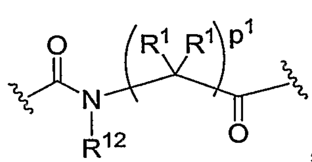
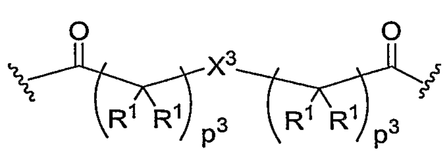
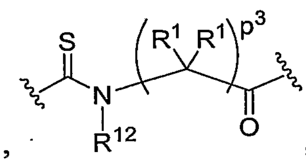
A^2 is alkyl, aryl, aralkyl,r -Si(R^3)$_3$,  ,  , or

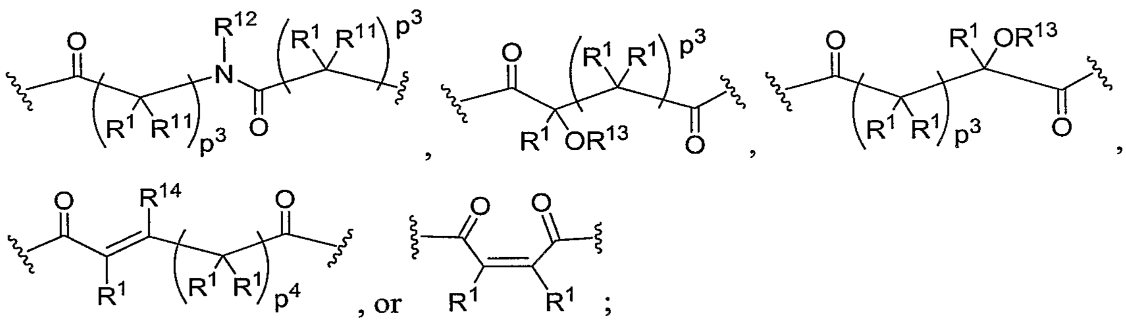
 ;

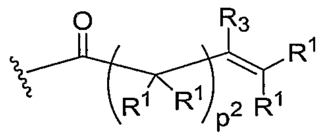
A^3 represents independently for each occurrence alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, heteroaryl, or aralkyl;

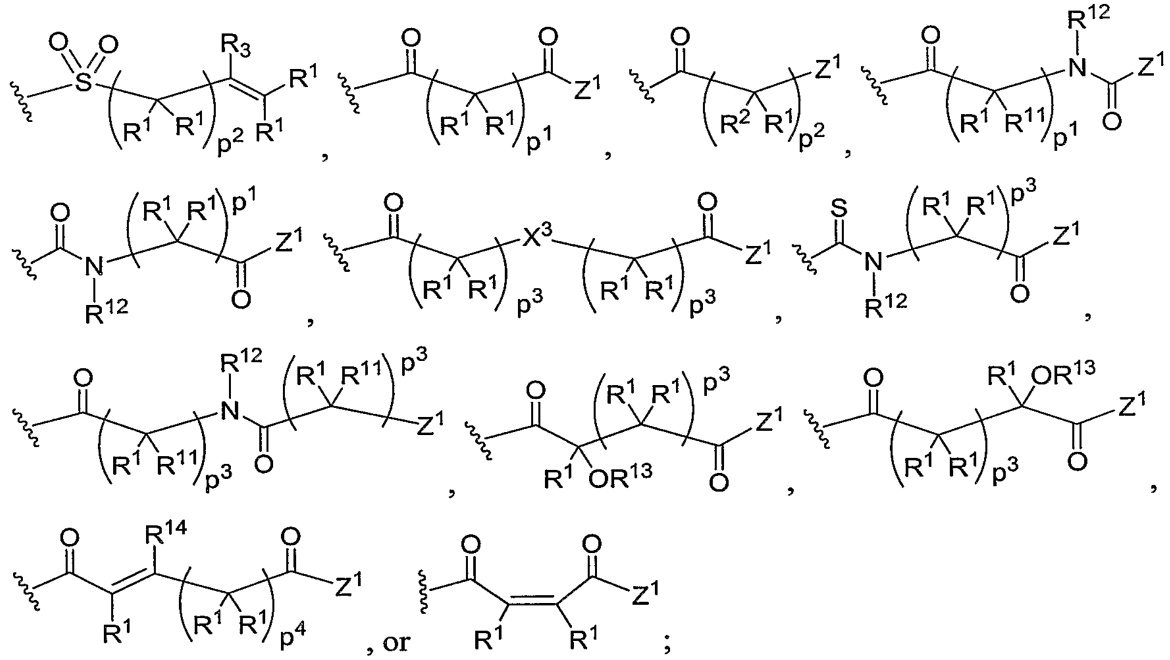
B is  ,  ,

 ,  ,

 ,  ,  ,

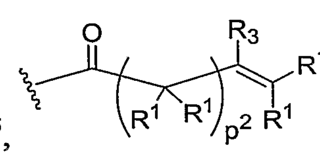


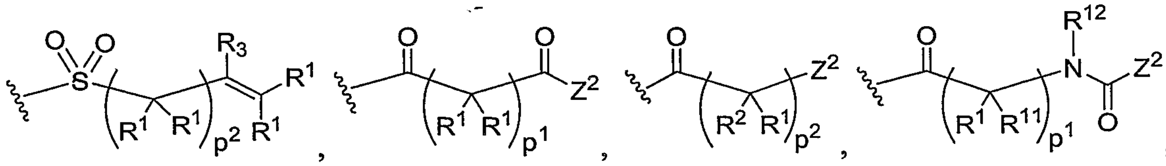
Y[1] represents independently for each occurrence R[4], ,

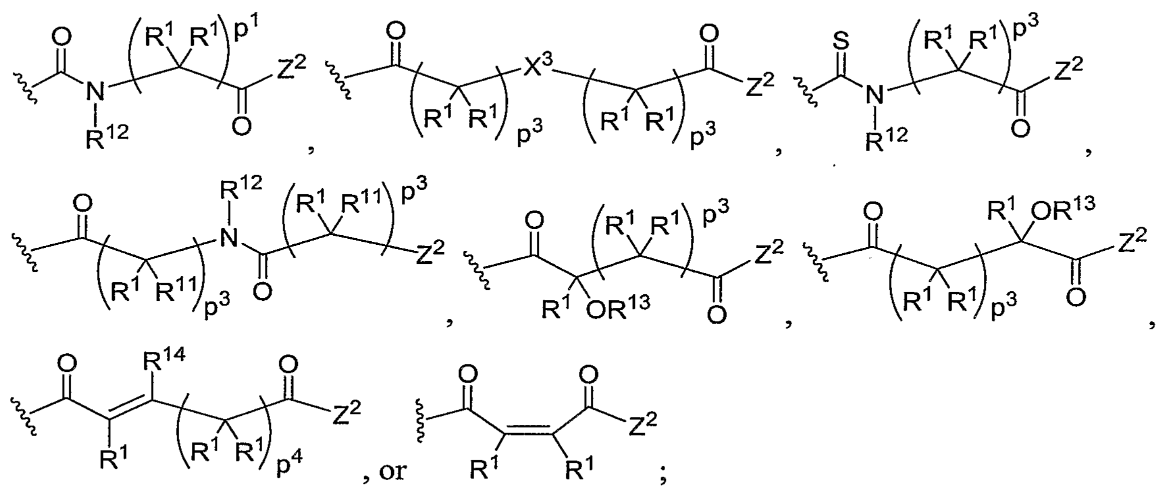


Z[1] represents independently for each occurrence -X[1]-R[4], E, or

$\text{-}X^1\text{-}A^3\text{-}(X^2\text{-}Y^2)_t$;

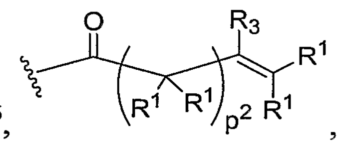
Y[2] represents independently for each occurrence R[5], ,

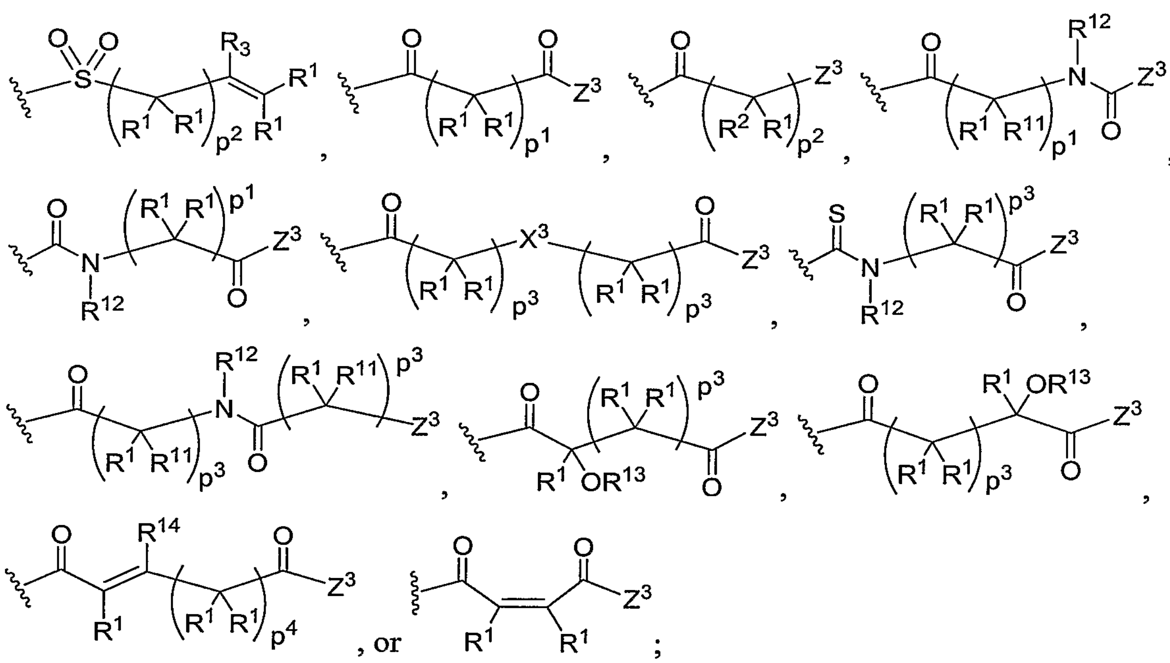




Z^2 represents independently for each occurrence $-X^1-R^5$, E, or

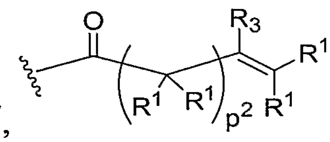
$-X^1-(A^3)-(X^2-Y^3)_t$;

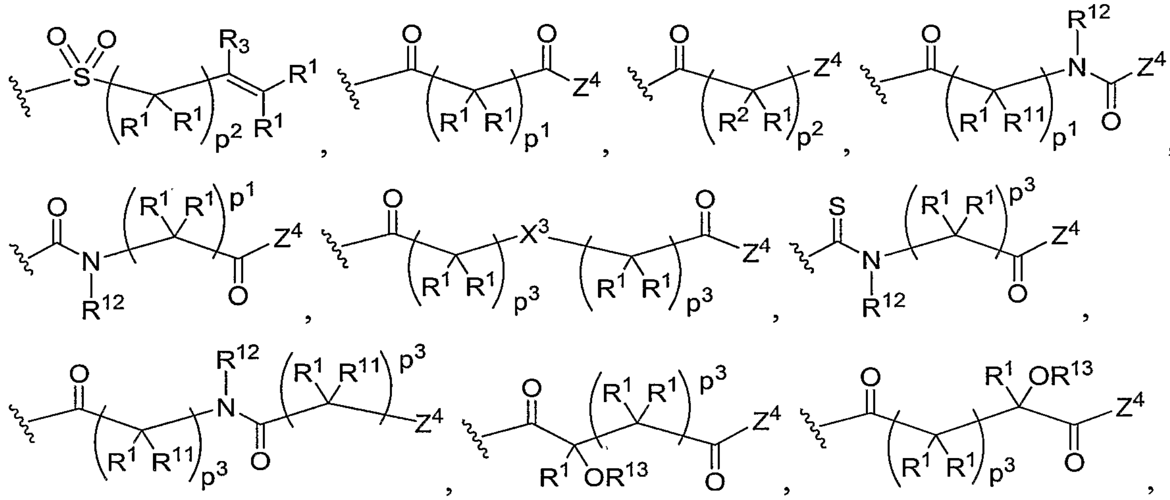
Y^3 represents independently for each occurrence R^6, ,

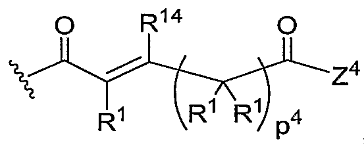
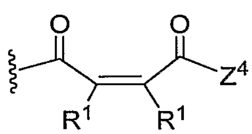


Z^3 represents independently for each occurrence $-X^1-R^6$, E, or

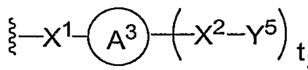
$-X^1-(A^3)-(X^2-Y^4)_t$;

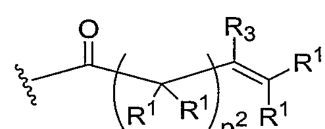
Y^4 represents independently for each occurrence R^7,  ,

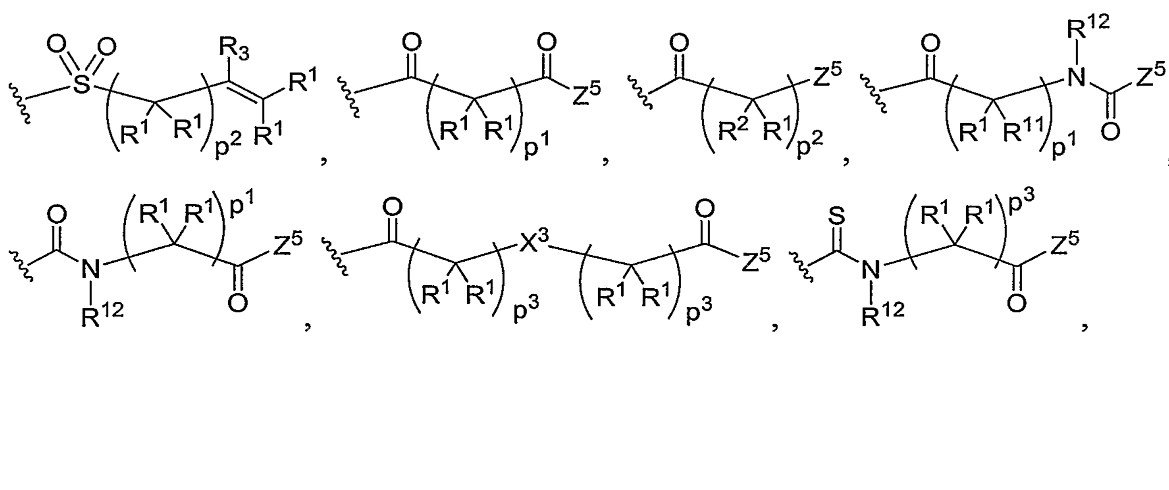


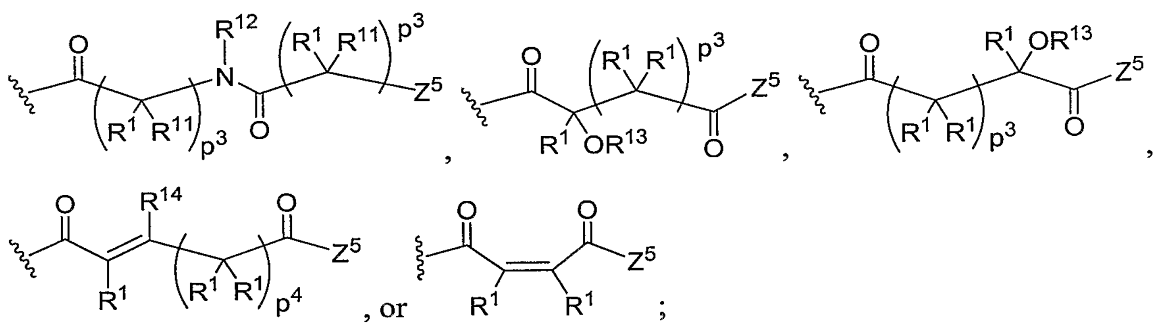
 , or  ;

Z^4 represents independently for each occurrence $-X^1-R^7$, E, or

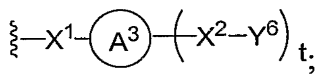
;

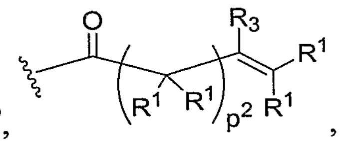
Y^5 represents independently for each occurrence R^8,  ,

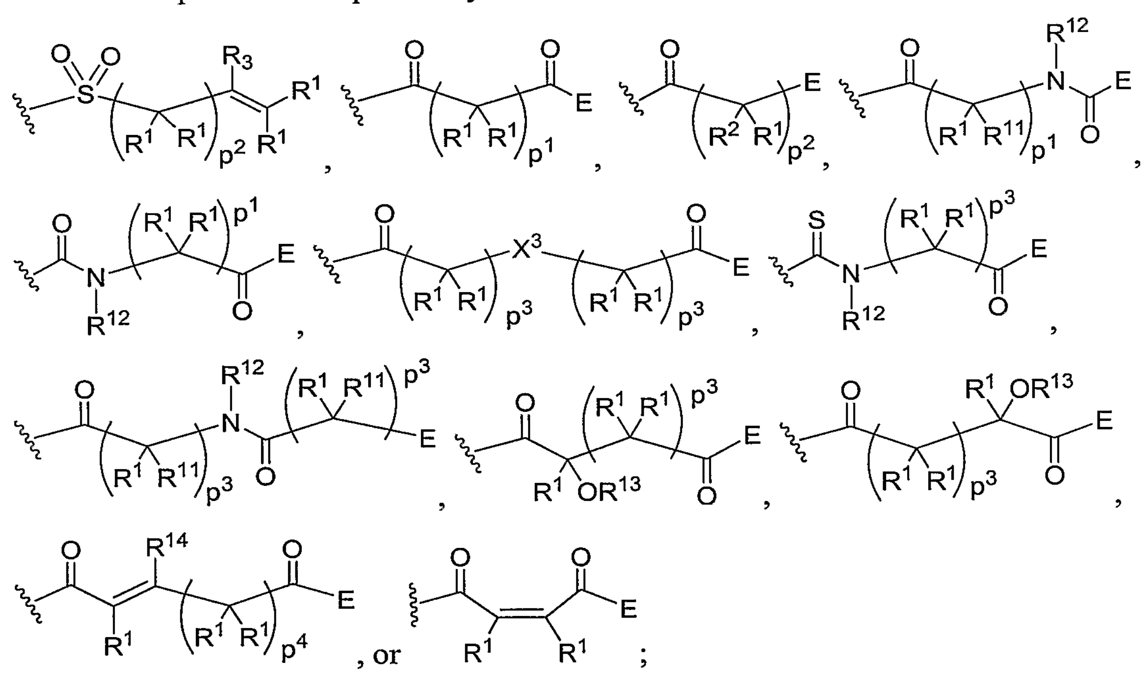




Z^5 represents independently for each occurrence $-X^1-R^8$, E, or



Y^6 represents independently for each occurrence R^9, 



R^1 represents independently for each occurrence H, alkyl, or halogen;

R^2 represents independently for each occurrence H, alkyl, -OH, $-N(R^{10})_2$, -SH, hydroxyalkyl, or $-[C(R^1)_2]_dR^{16}$;

R^3 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^4, R^5, R^6, R^7, R^8, and R^9 are H;

R^{10} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{11} represents independently for each occurrence H, -OH, -$N(R^{10})_2$, -SH, alkyl, hydroxyalkyl, or -$[C(R^1)_2]_dR^{16}$;

R^{12} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{13} represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^{14} represents independently for each occurrence H, alkyl, or -CO_2R^{10};

R^{15} represents independently for each occurrence H, alkyl, or -OR^{10};

R^{16} represents independently for each occurrence phenyl, hydroxyphenyl, pyrrolidyl, imidazolyl, indolyl, -$N(R^{10})_2$, -SH, -S-alkyl, -CO_2R^{10}, -$C(O)N(R^{10})_2$, or -$C(NH_2)N(R^{10})_2$;

n represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

p^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7; or 8;

p^2 represents independently for each occurrence 0, 1, 2, 3, or 4;

p^3 represents independently for each occurrence 1, 2, or 3;

p^4 represents independently for each occurrence 0, 1, 2, or 3;

d represents independently for each occurrence 1, 2, 3, 4, 5, or 6;

t represents independently for each occurrence 2, 3, 4, or 5 in accord with the rules of valence;

v^1 and v^2 each represent independently for each occurrence 2, 3, or 4;

w^1 and w^2 each represent independently for each occurrence an integer from about 5 to about 700, inclusive;

x is 1, 2, or 3;

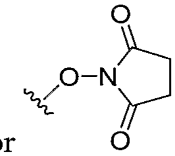
y is 0, 1, 2, 3, 4, or 5;

z^1 represents independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

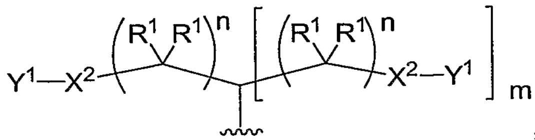
z^2 and z^3 each represent independently for each occurrence 1, 2, 3, 4, or 5;

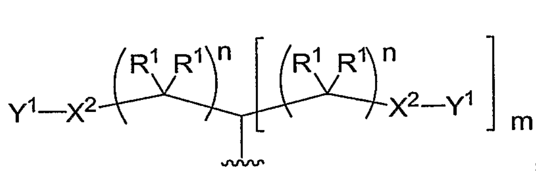
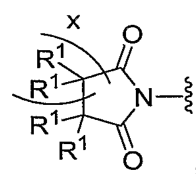
X^1 and X^2 each represent independently for each occurrence O or -$N(R^{10})$-;

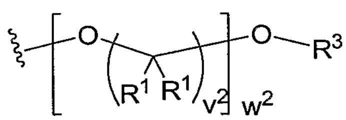
X^3 represents independently for each occurrence O, $N(R^{10})$, or $C(R^{15})(CO_2R^{10})$; and

E represents independently for each occurrence H, $-[C(R^1)_2]_nC(O)H$, or  .

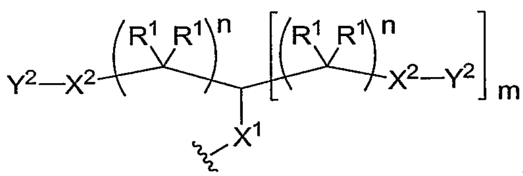
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is ultraviolet light, visible light, a compound of formula **II**, a compound of formula **III**, or an oxidizing agent.

In certain instances, the present invention relates to the aforementioned method, wherein A^1 is  , and m is 1 or 2.

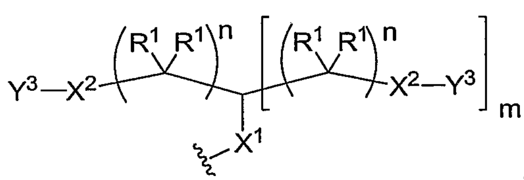
In certain instances, the present invention relates to the aforementioned method, wherein A^2 is  ,  ,

 , or $-Si(R^3)_3$; wherein, m is 1 or 2.

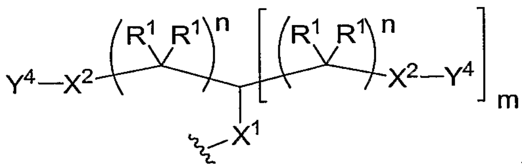
In certain instances, the present invention relates to the aforementioned method, wherein Z^1 represents independently for each occurrence $-X^1-R^4$ or

 , and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^2 represents independently for each occurrence $-X^1-R^5$ or

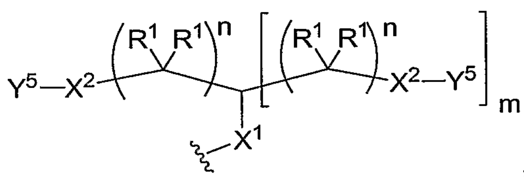
 , and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^3 represents independently for each occurrence $-X^1-R^6$ or



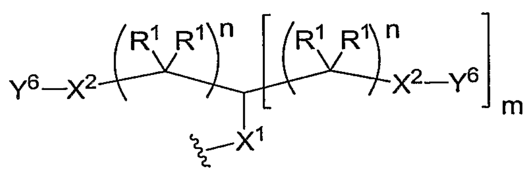
, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^4 represents independently for each occurrence $-X^1-R^7$ or



, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein Z^5 represents independently for each occurrence $-X^1-R^8$ or



, and m is 1 or 2.

In certain instances, the present invention relates to the aforementioned method, wherein X^1 is O.

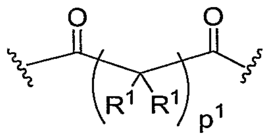
In certain instances, the present invention relates to the aforementioned method, wherein X^1 and X^2 are O.

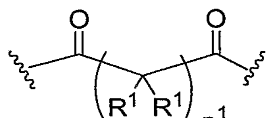
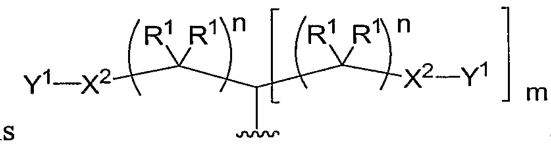
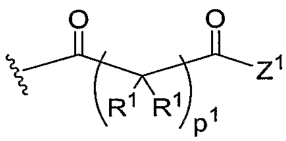
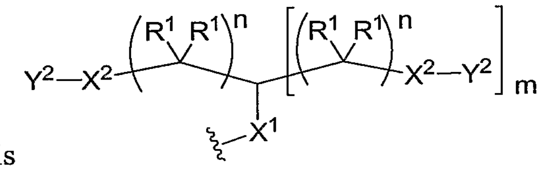
In certain instances, the present invention relates to the aforementioned method, wherein n is 1.

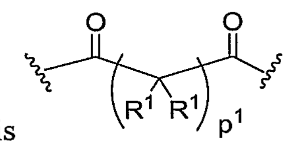
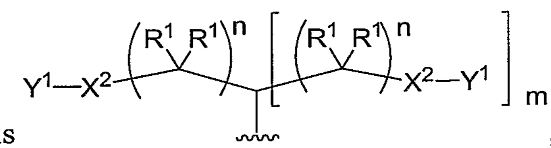
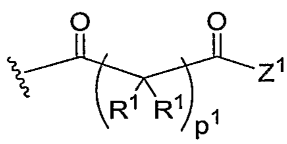
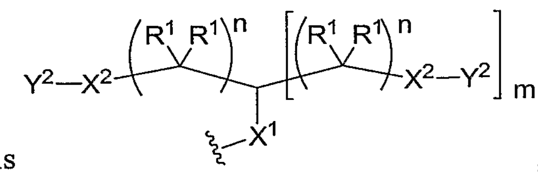
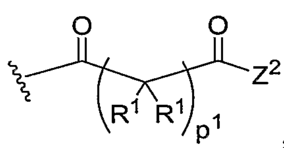
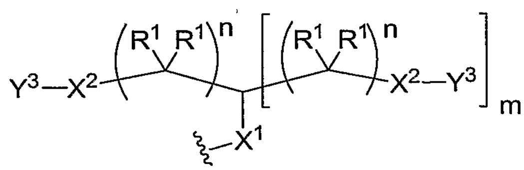
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, 3, or 4.

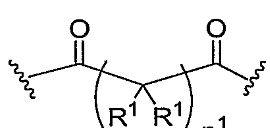
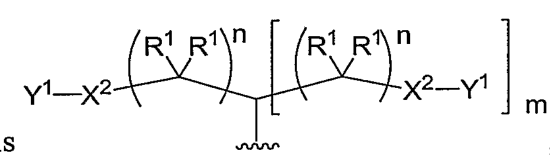
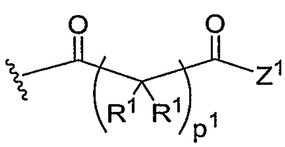
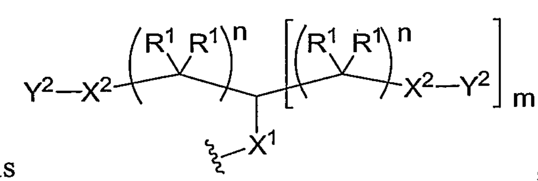
In certain instances, the present invention relates to the aforementioned method, wherein p^2 is 1.

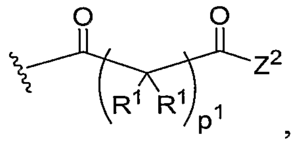
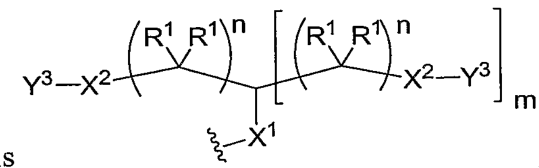
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H.

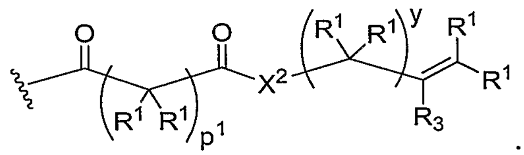
In certain instances, the present invention relates to the aforementioned method, wherein B is .

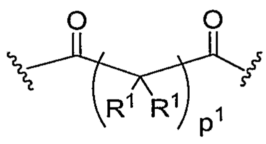
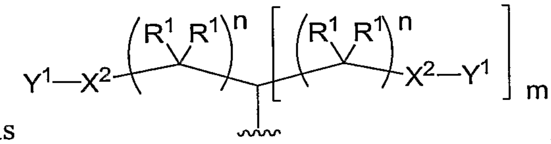
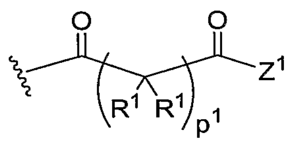
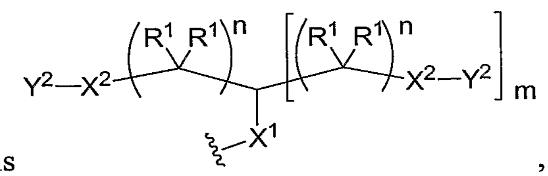
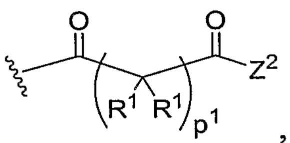
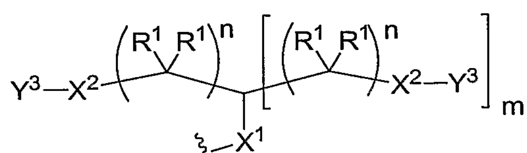
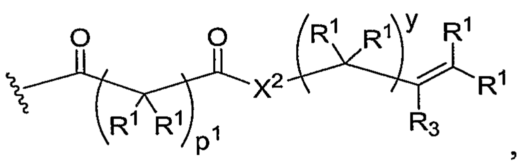
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , and Z^1 is .

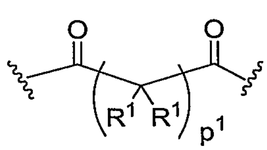
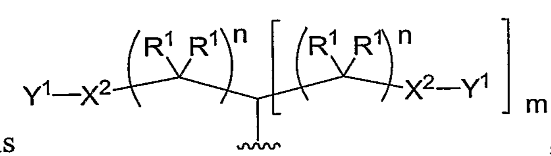
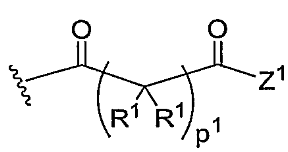
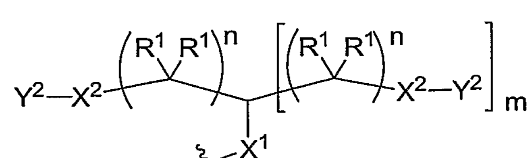
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is .

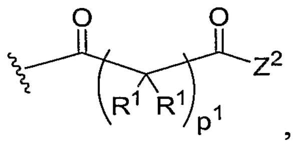
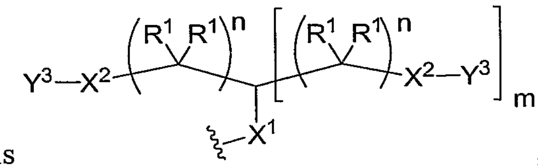
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

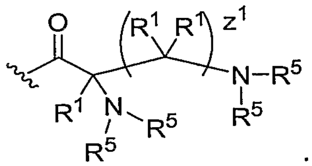
 , Z^2 is  , and Y^3 is

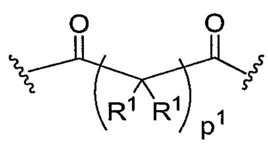
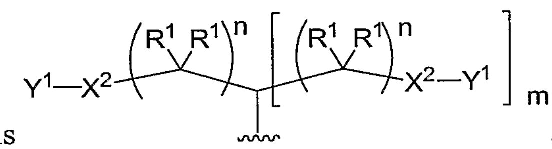
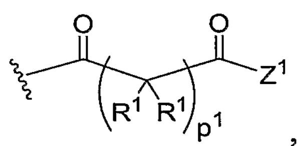
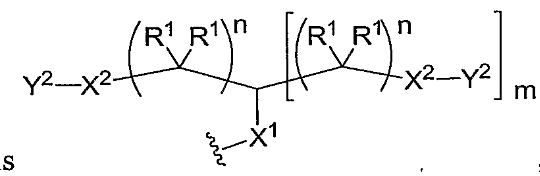
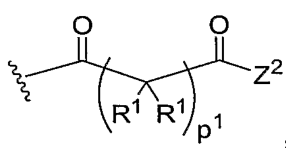
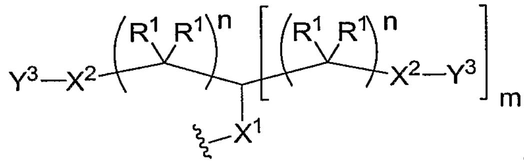
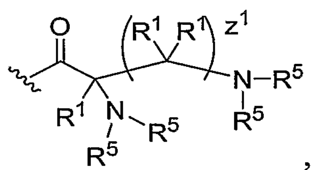
 .

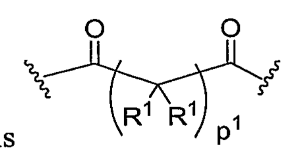
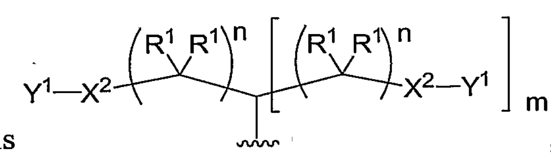
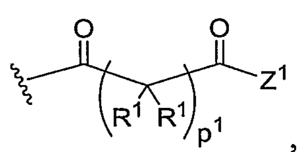
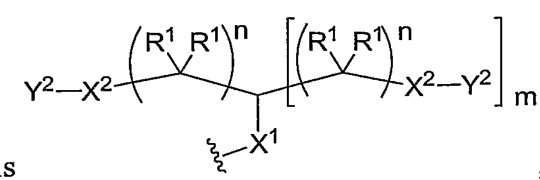
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and said polymerization agent is ultraviolet light or visible light.

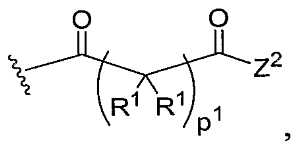
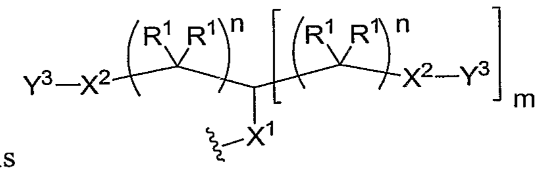
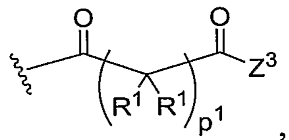
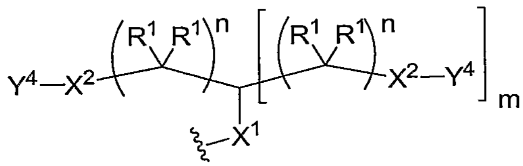
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is

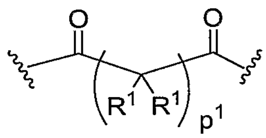
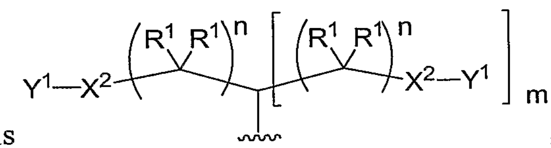
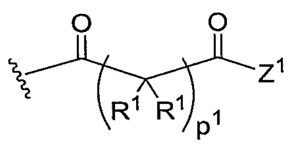
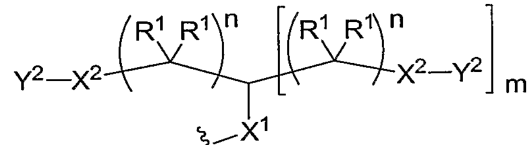
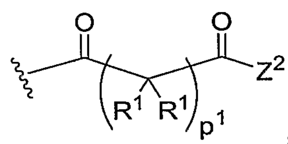
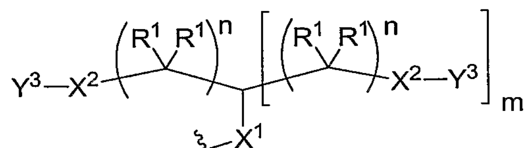
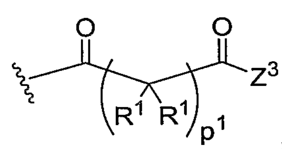
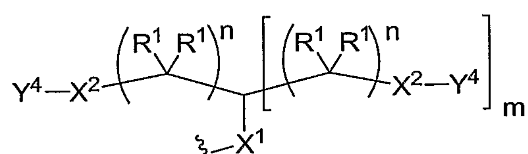
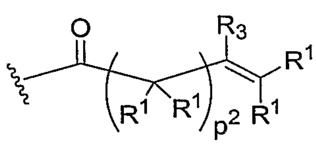
, Z^2 is , and Y^3 is

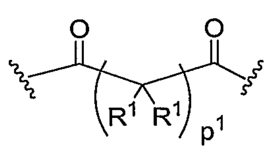
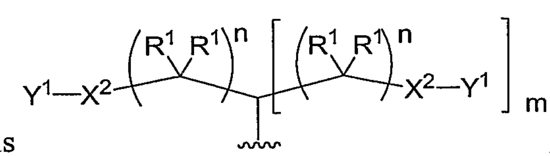
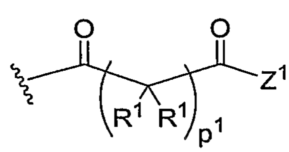
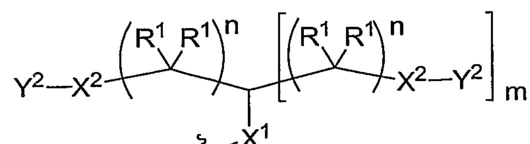
.

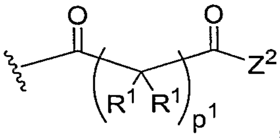
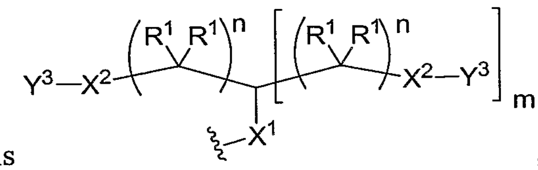
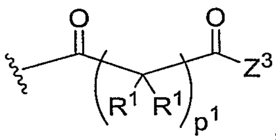
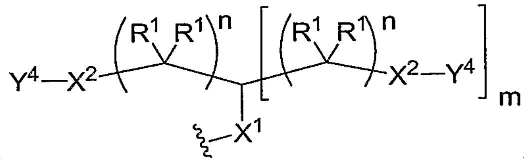
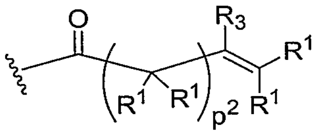
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is a compound of formula **III**.

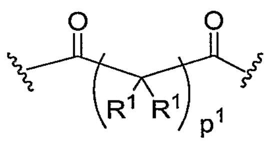
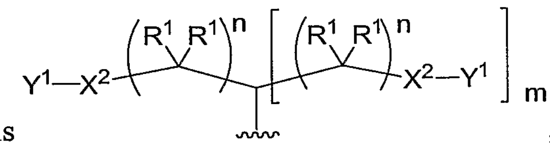
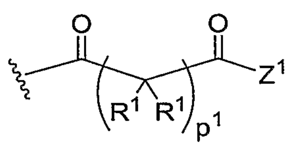
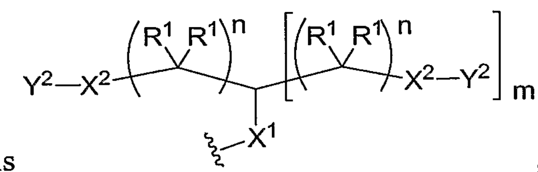
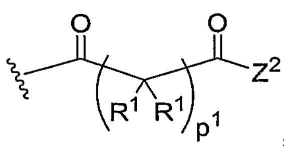
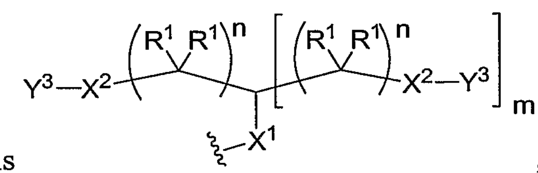
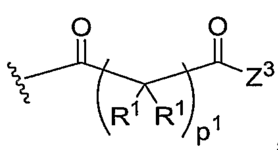
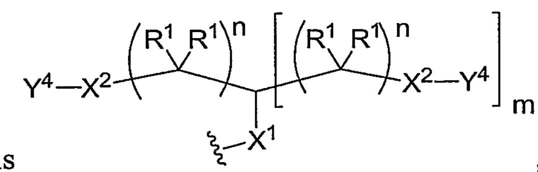
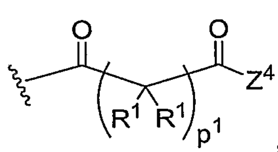
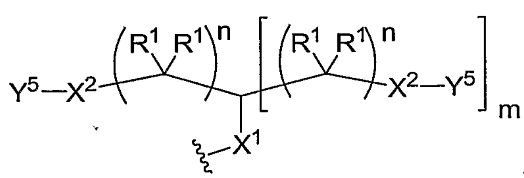
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

, Z^2 is , Y^3 is , and Z^3 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , and at least about 1/2 of the Y^4 groups are .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is

, Z^2 is , Y^3 is , Z^3 is , at least about 1/2 of the Y^4 groups are , and said polymerization agent is ultraviolet light or visible light.

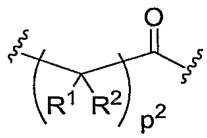
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , and Z^4 is .

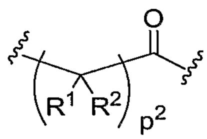
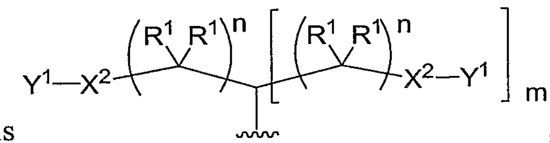
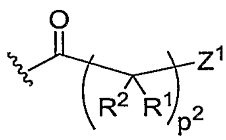
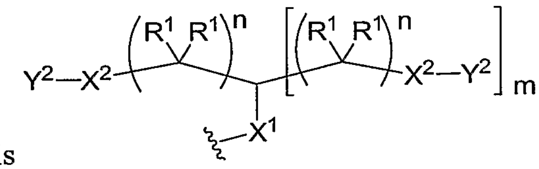
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 1, 2, 3, or 4.

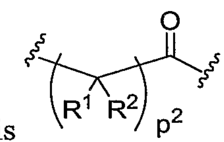
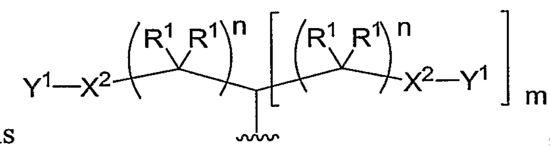
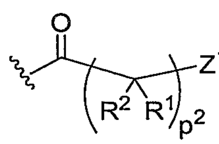
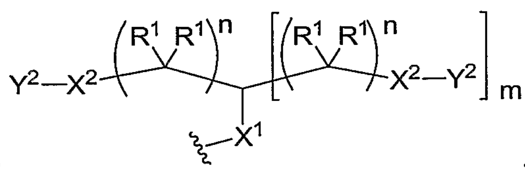
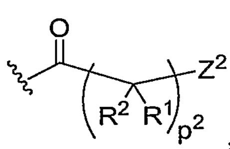
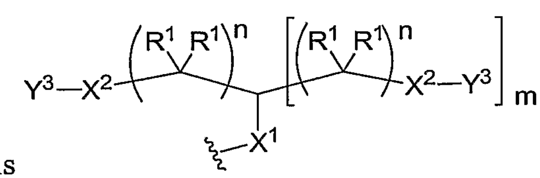
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

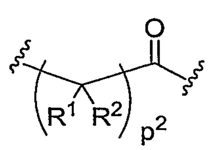
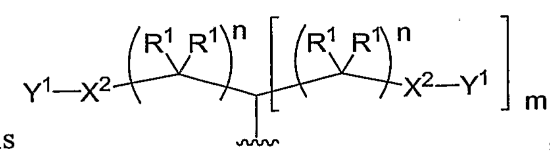
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 4.

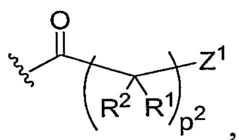
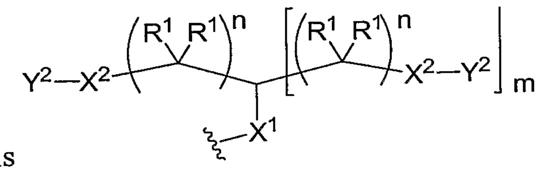
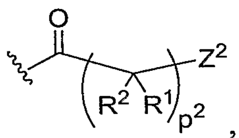
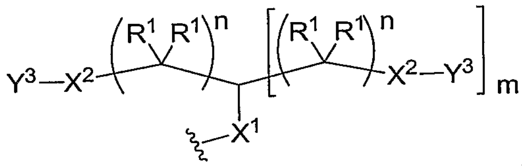
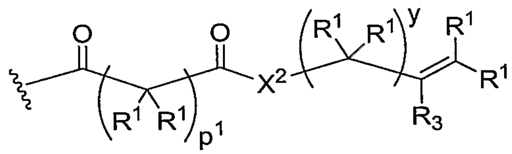
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

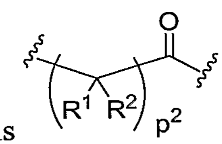
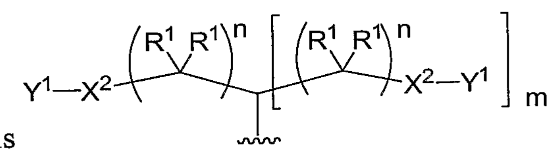
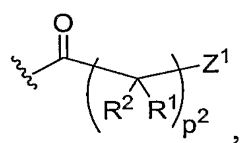
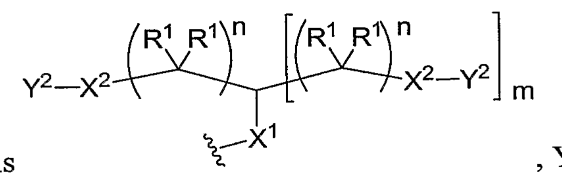
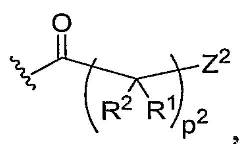
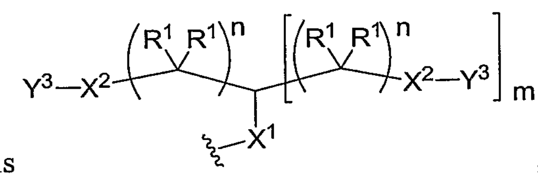
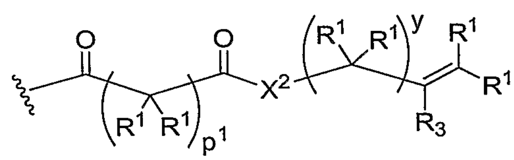
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

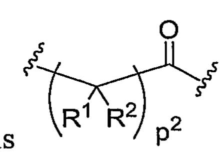
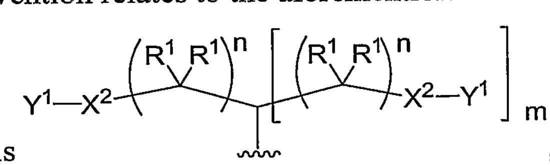
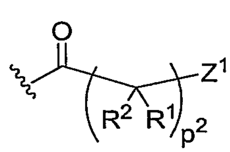
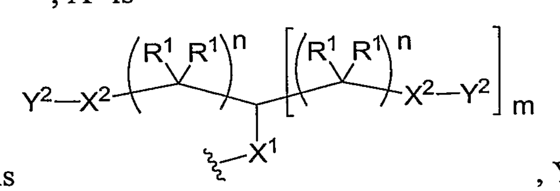
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

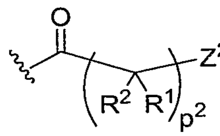
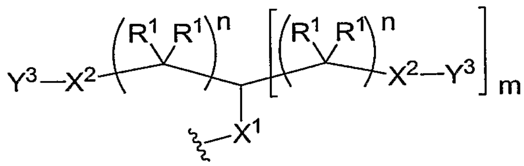
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is  .

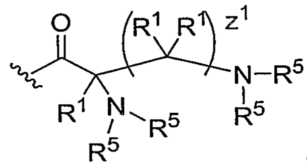
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1

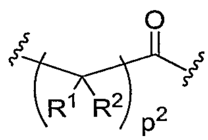
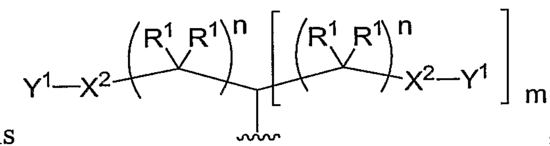
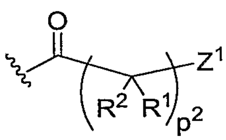
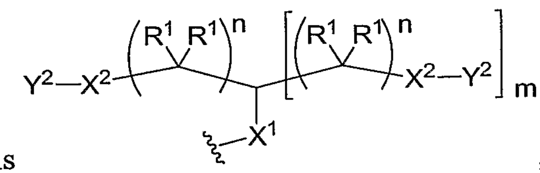
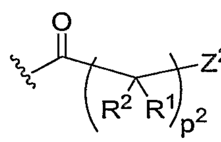
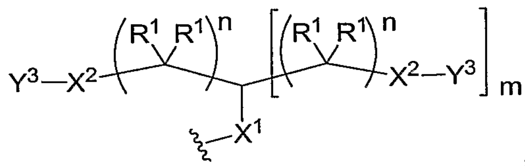
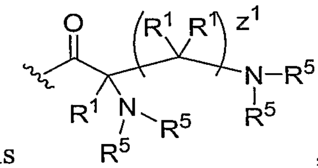
or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , and Y^3 is  .

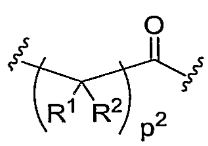
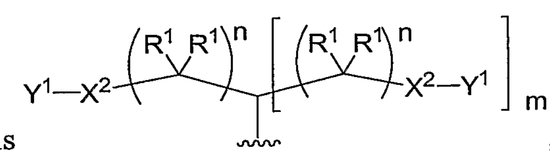
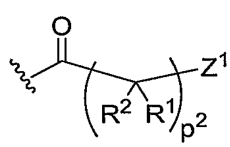
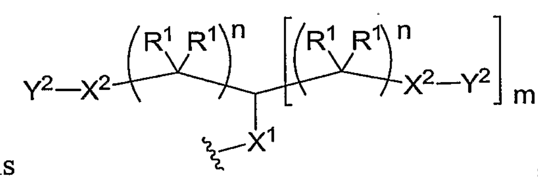
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and said polymerization agent is ultraviolet light or visible light.

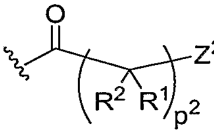
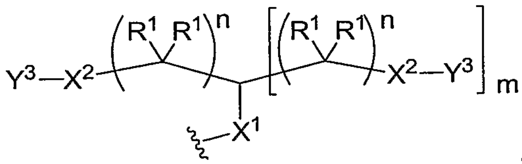
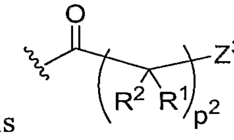
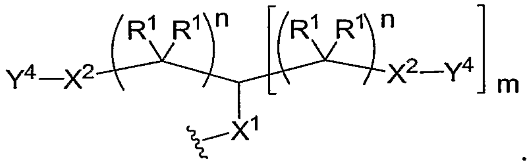
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is

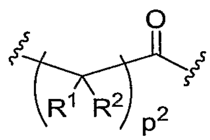
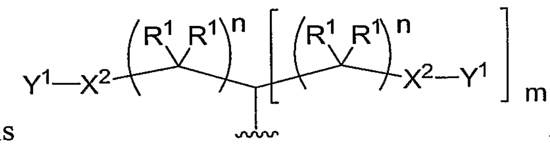
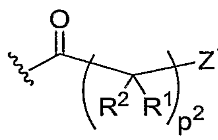
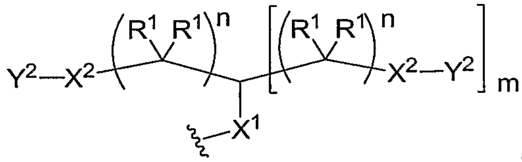
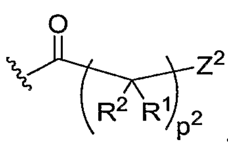
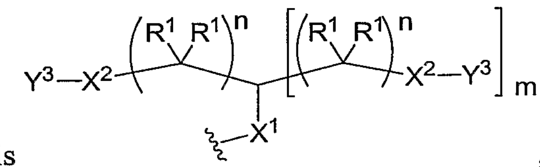
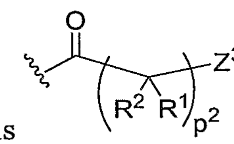
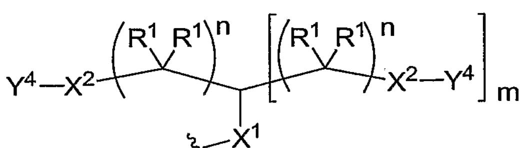
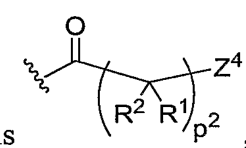
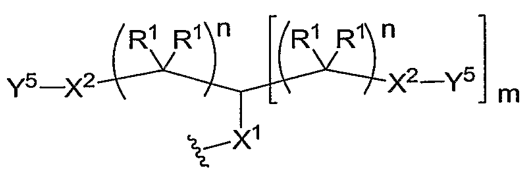
 , Z^2 is  , and Y^3 is

 .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , and said polymerization agent is a compound of formula **III**.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is

 , Z^2 is  , Y^3 is  , and Z^3 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is  , and Z^4 is  .

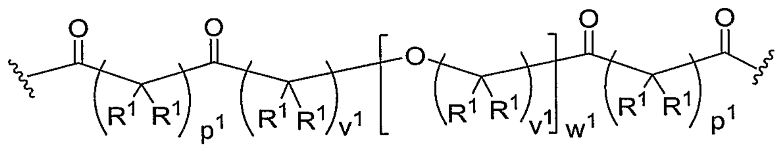
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 1, 2, 3, or 4.

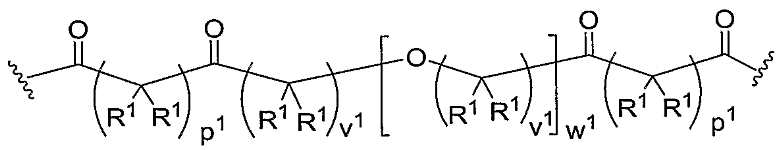
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

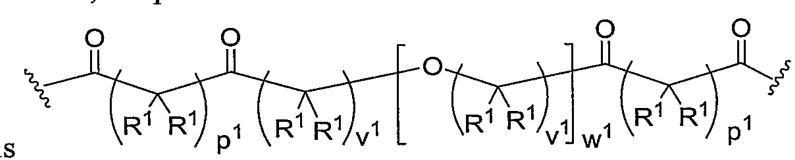
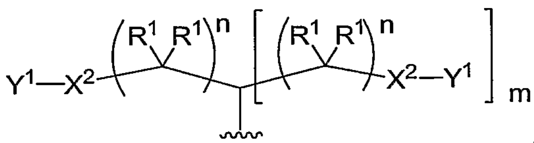
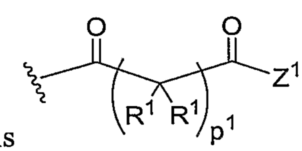
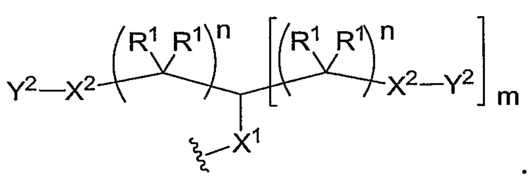
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 4.

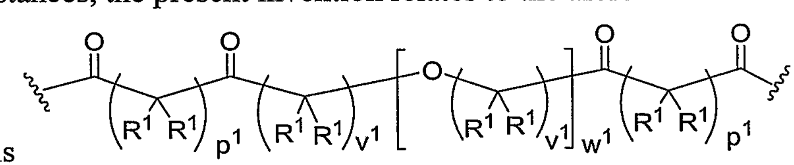
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

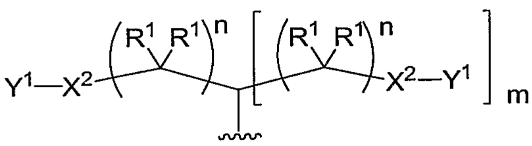
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is $(C_1\text{-}C_3)$alkyl.

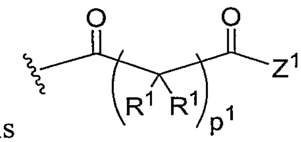
In certain instances, the present invention relates to the aforementioned method, wherein B is  .

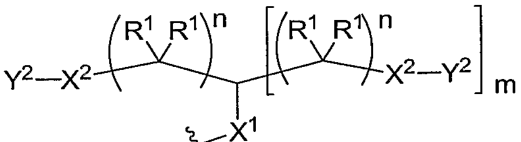
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , and v^1 is 2.

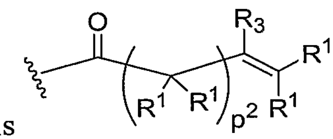
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  .

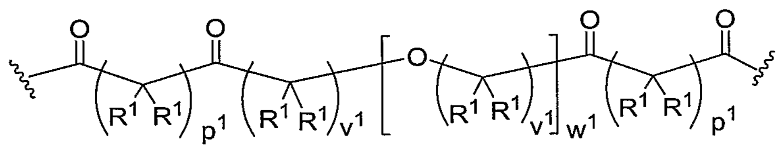
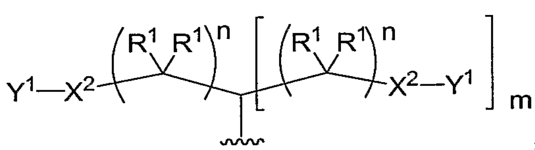
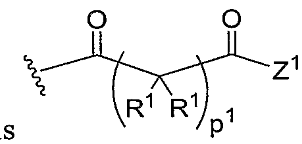
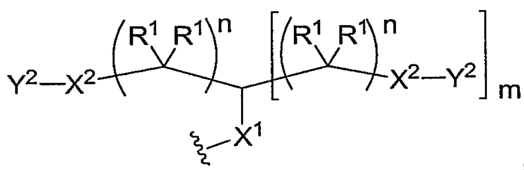
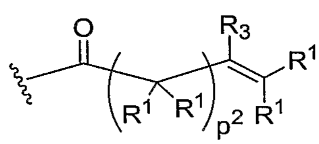
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2

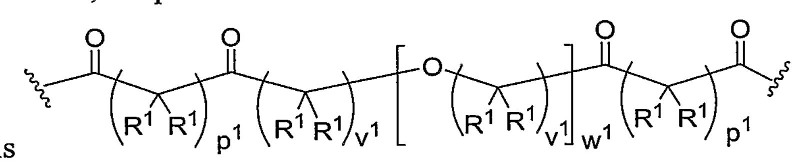
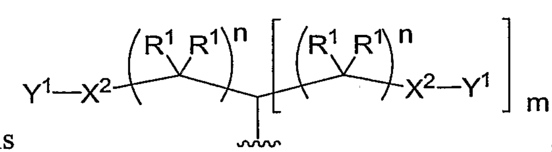
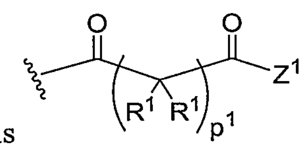
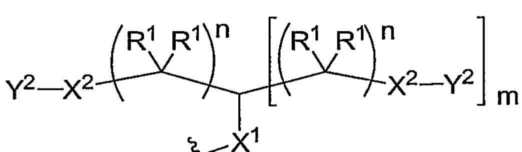
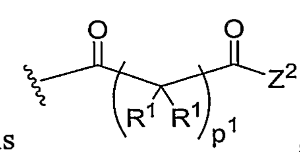


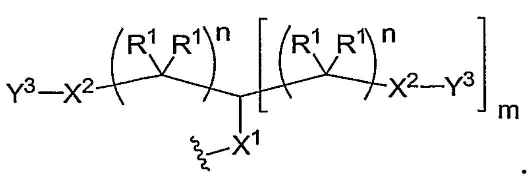
is , m is 1 or 2, Y^1 is  , Z^1 is



, and Y^2 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , and Z^1 is  , Y^2 is  , and said polymerization agent is ultraviolet light or visible light.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , and Z^2 is



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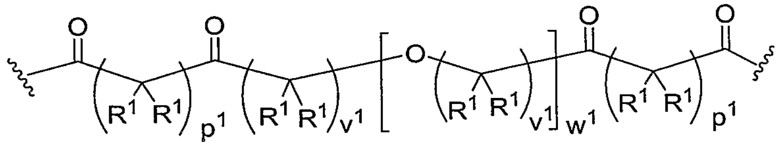
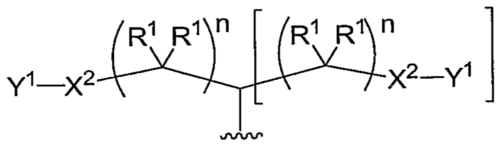
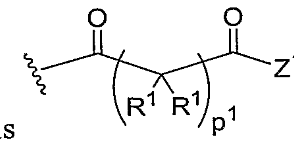
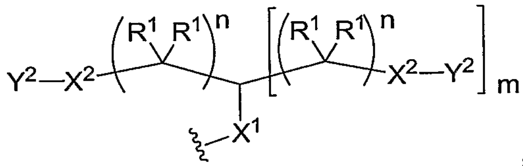
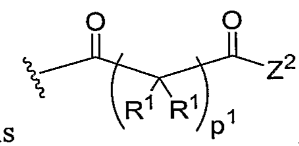
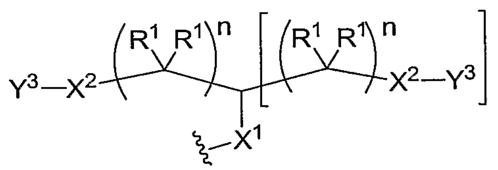
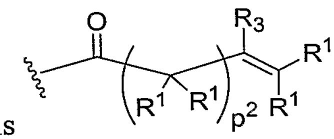
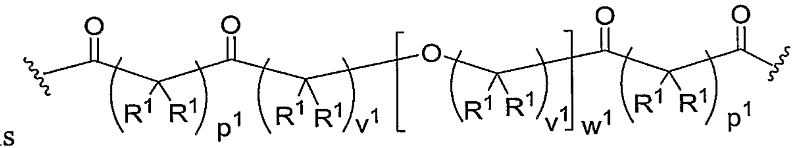
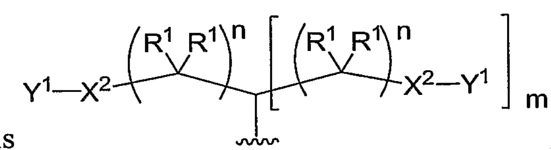
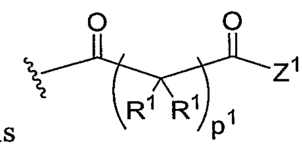
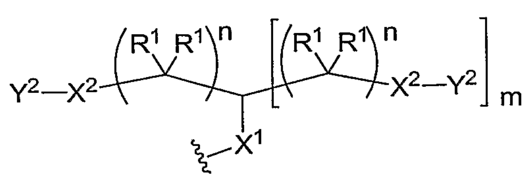
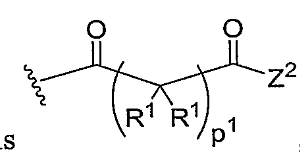
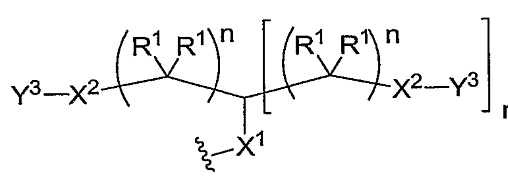
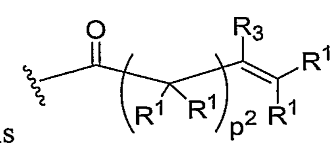
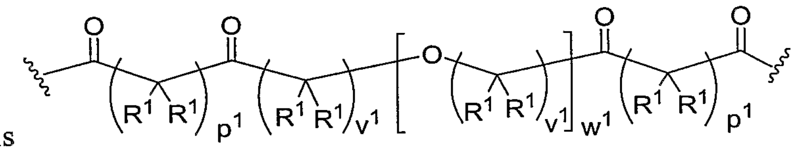
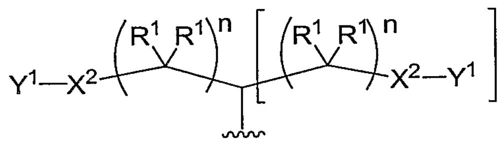
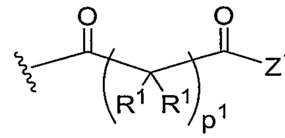
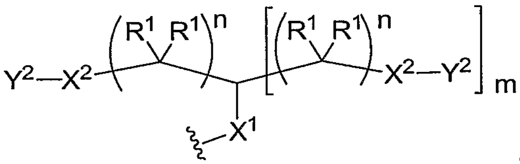
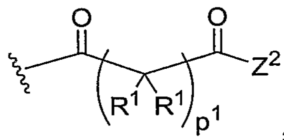
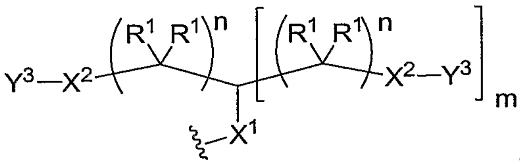
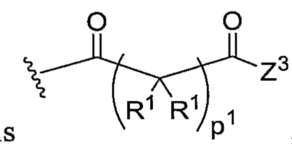
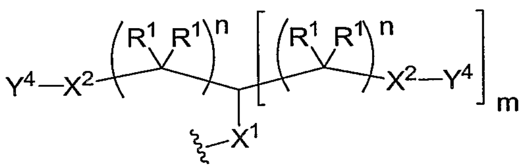
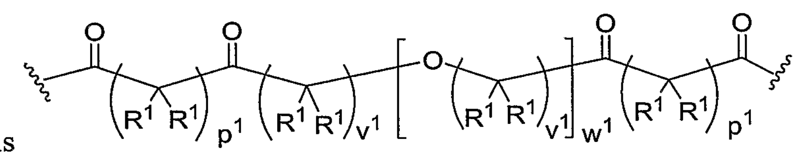
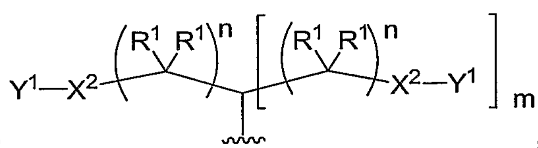
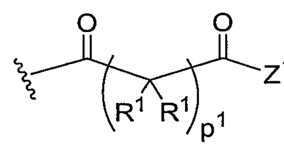
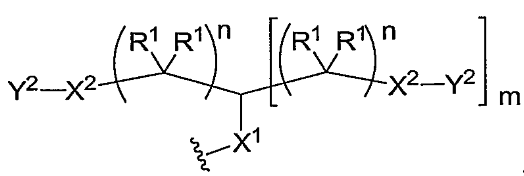
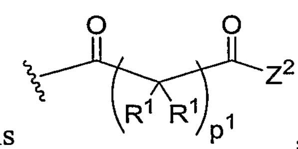
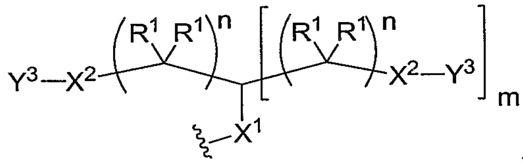
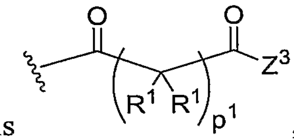
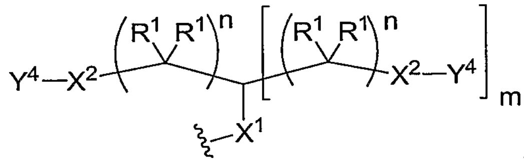
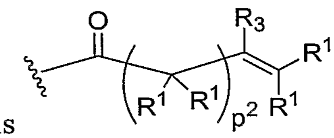
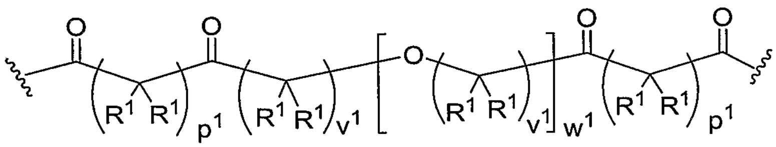
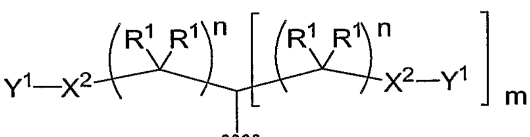
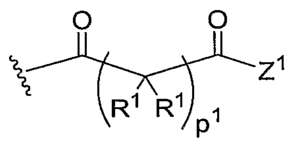
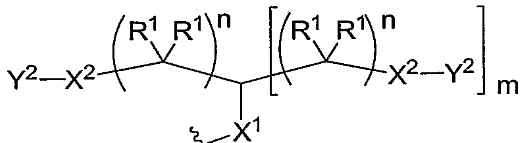
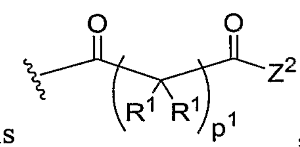
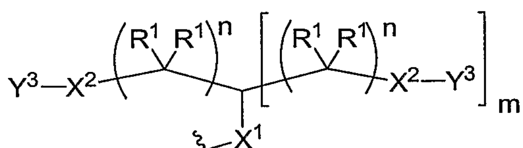
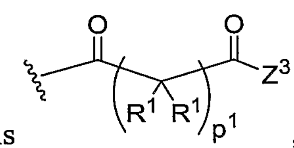
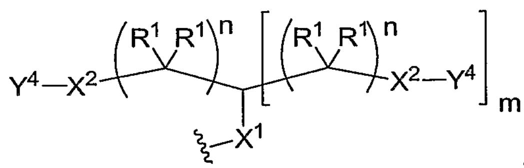
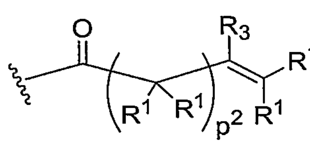
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

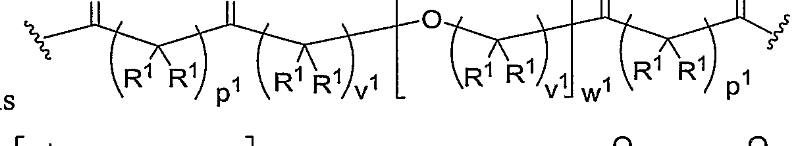
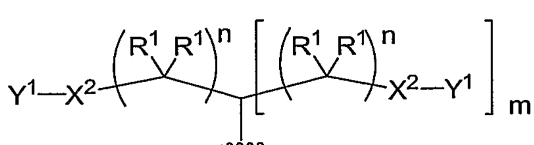
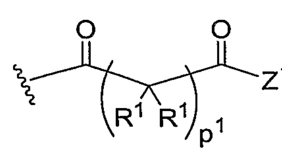
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and said polymerization agent is ultraviolet light or visible light.

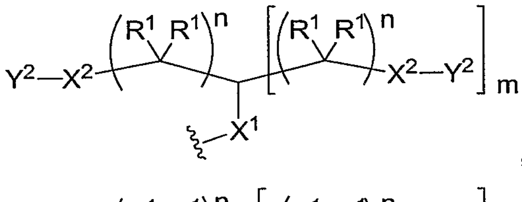
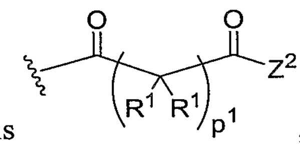
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and Z^3 is .

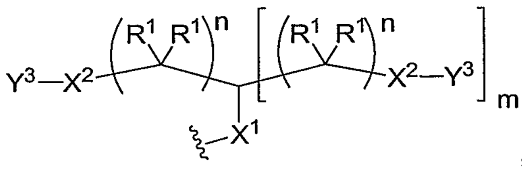
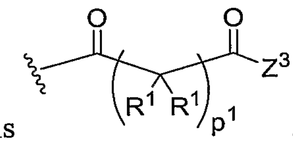
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is

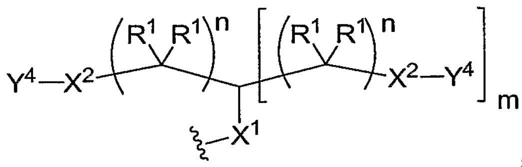
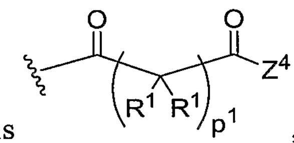
 , Y^3 is  , Z^3 is  , and Y^4 is  .

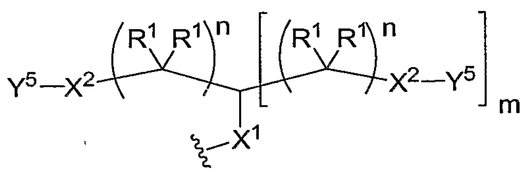
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is  , and said polymerization agent is ultraviolet light or visible light.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , v^1 is 2, A^2 is  , m is 1 or 2, Y^1 is  , Z^1 is

, Y^2 is , Z^2 is

, Y^3 is , Z^3 is

, Y^4 is , and Z^4 is

.

In certain instances, the present invention relates to the aforementioned method, wherein w^1 is an integer in the range of about 50 to about 250.

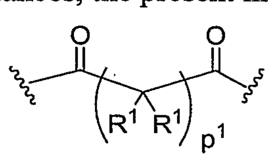
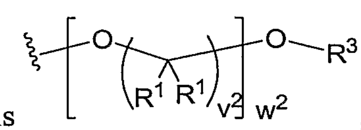
In certain instances, the present invention relates to the aforementioned method, wherein w^1 is an integer in the range of about 60 to about 90.

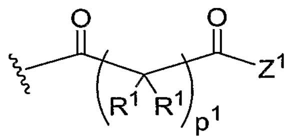
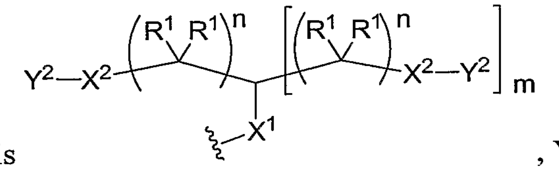
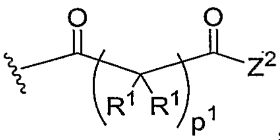
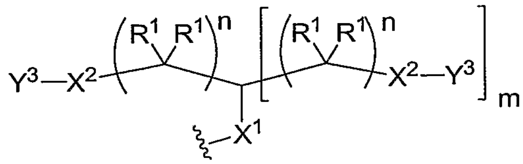
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

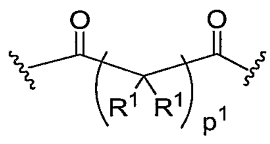
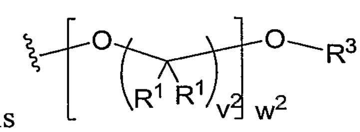
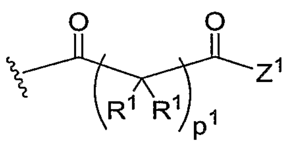
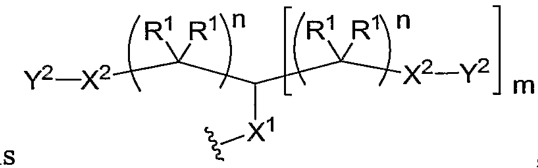
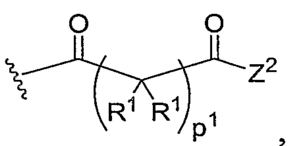
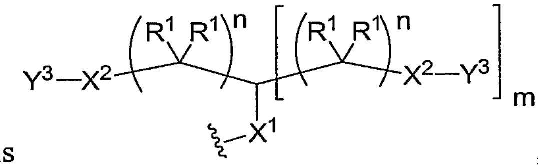
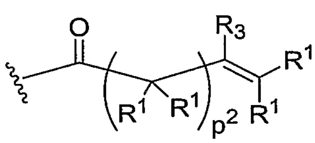
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

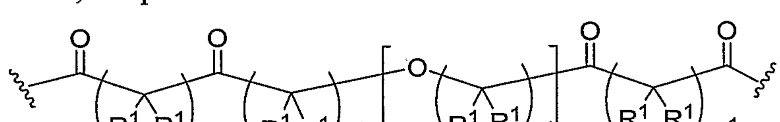
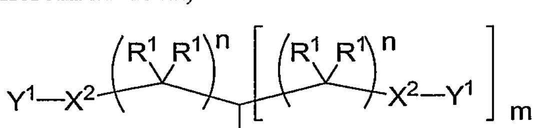
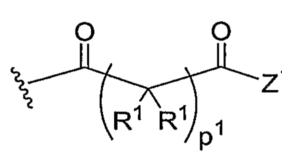
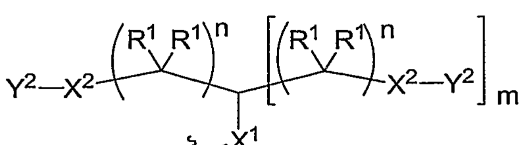
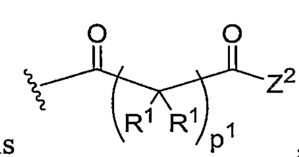
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl.

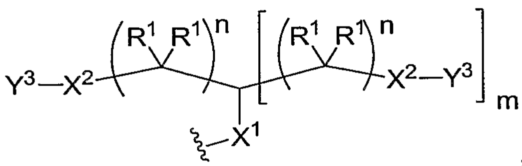
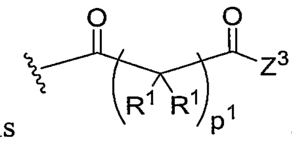
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, R^3 is $(C_1\text{-}C_5)$alkyl, and w^1 is an integer in the range of about 60 to about 90.

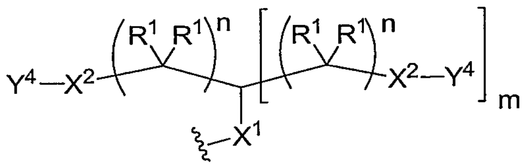
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is

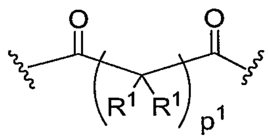
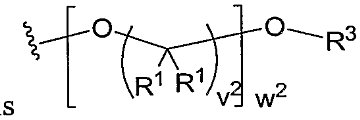
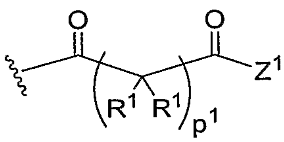
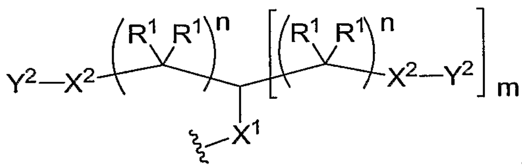
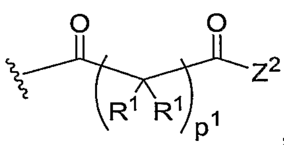
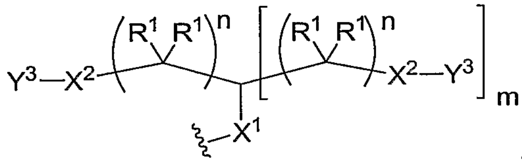
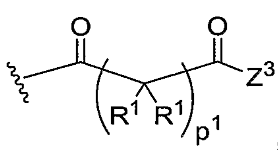
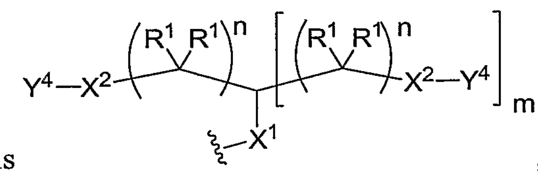
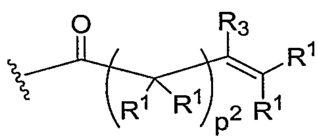
2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is .

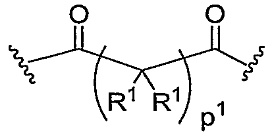
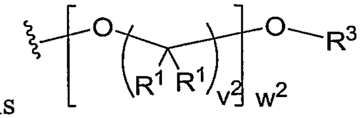
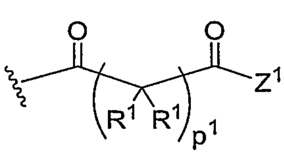
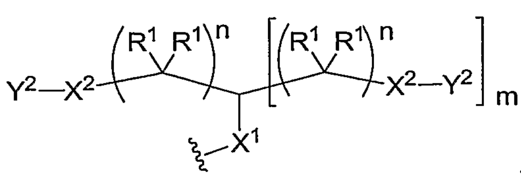
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , and Y^3 is .

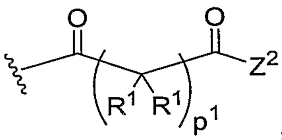
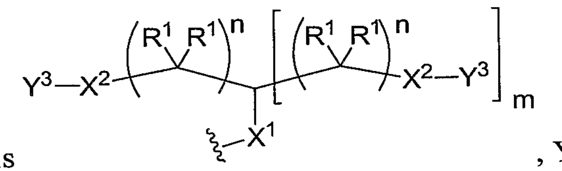
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , v^1 is 2, A^2 is , m is 1 or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is

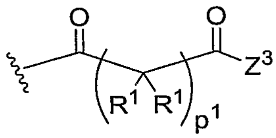
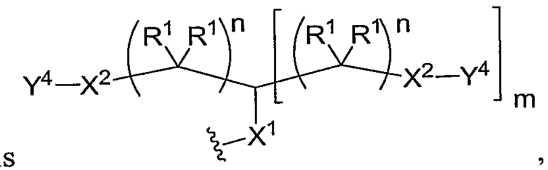
, Y^3 is , and Z^3 is

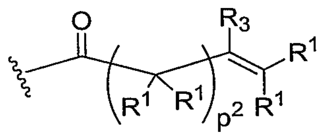
.

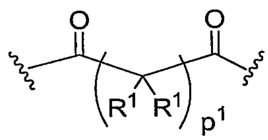
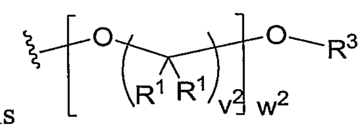
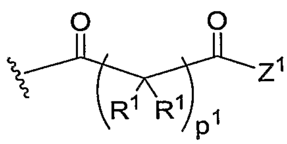
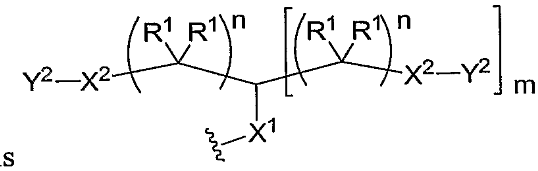
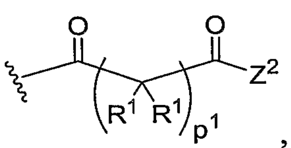
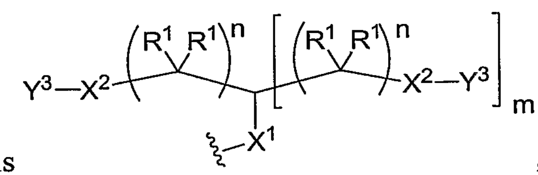
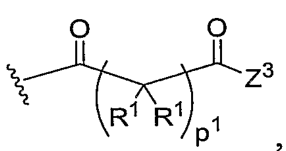
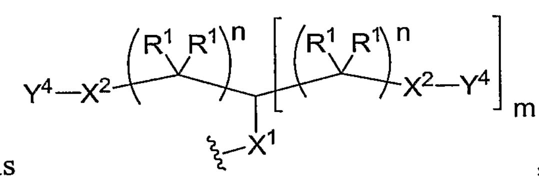
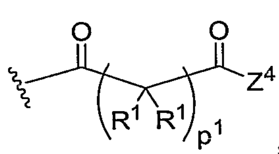
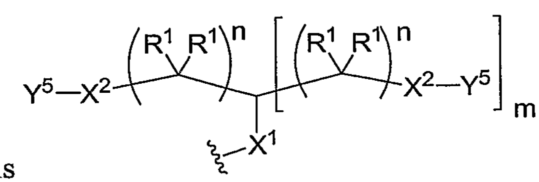
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , and Y^4 is .

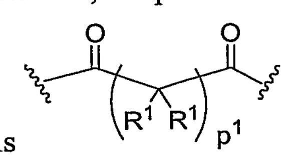
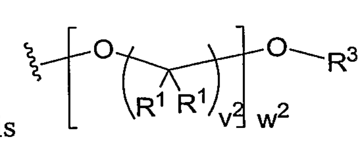
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is

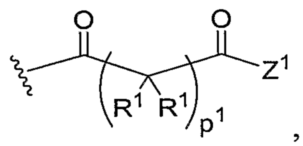
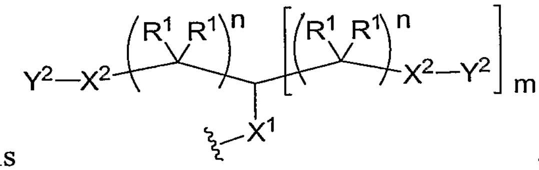
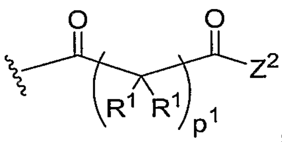
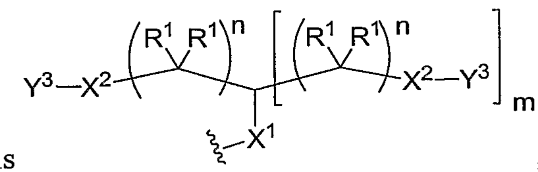
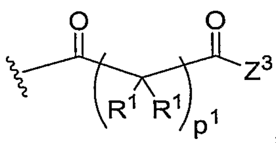
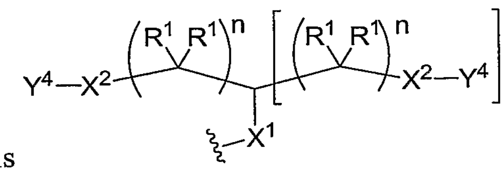
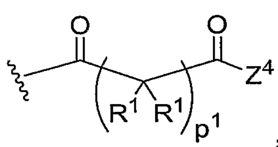
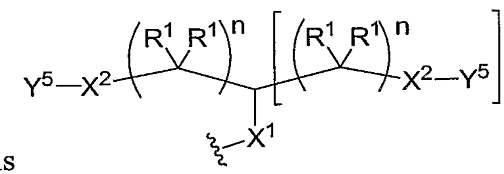
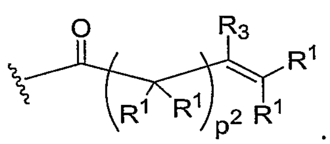
, Z^2 is , Y^3 is

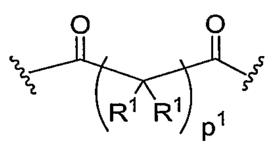
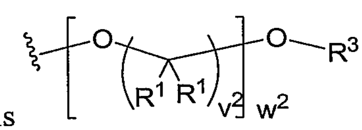
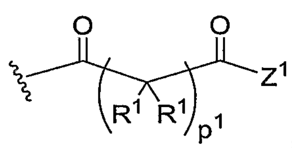
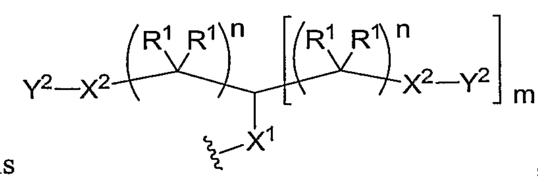
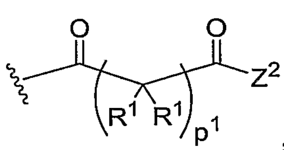
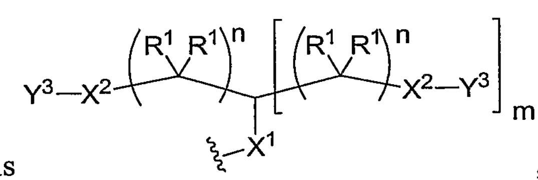
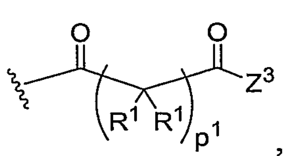
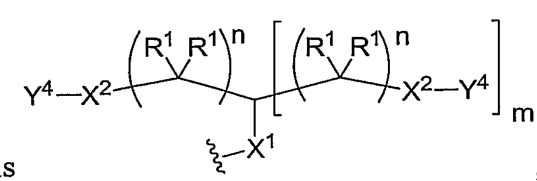
, Z^3 is , Y^4 is

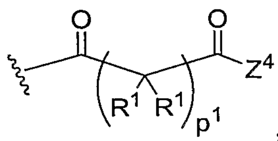
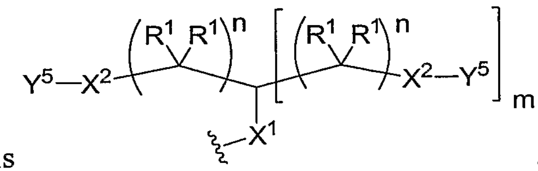
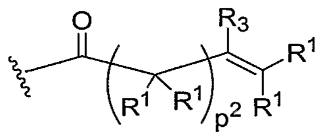
, and said polymerization agent is ultraviolet light or visible light.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , Z^3 is , Y^4 is , and Z^4 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , R^3 is alkyl, v^2 is

2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is  , Z^4 is  , and Y^5 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is  , A^2 is  , R^3 is alkyl, v^2 is 2, Y^1 is  , Z^1 is  , Y^2 is  , Z^2 is  , Y^3 is  , Z^3 is  , Y^4 is

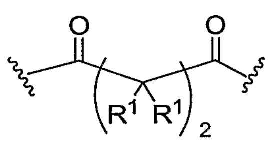
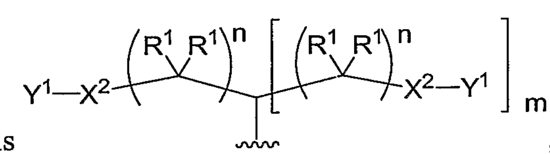
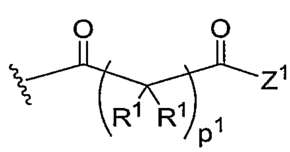
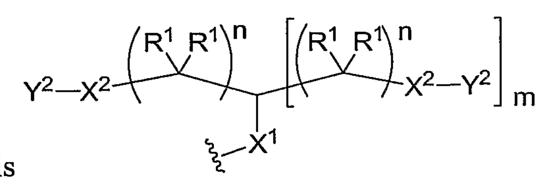
, Z^4 is , Y^5 is , and said polymerization agent is ultraviolet light or visible light.

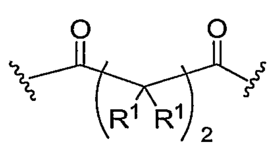
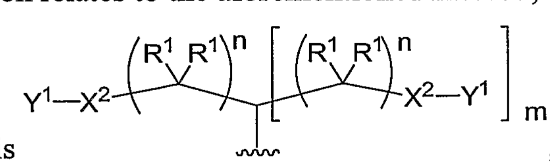
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2.

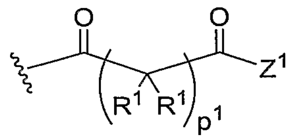
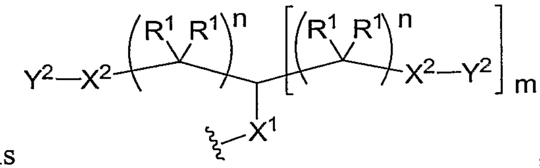
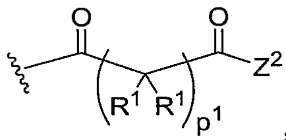
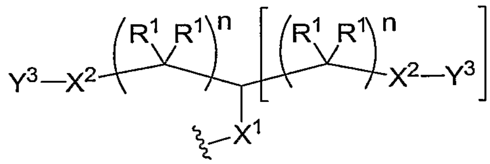
In certain instances, the present invention relates to the aforementioned method, wherein m is 1.

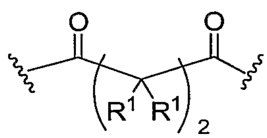
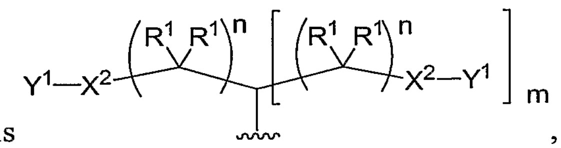
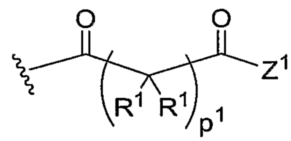
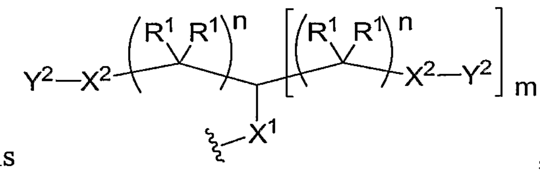
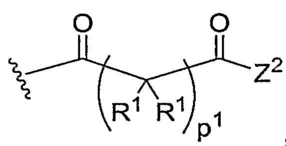
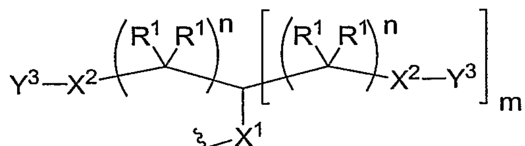
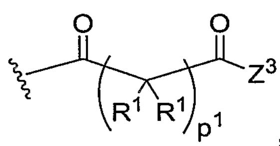
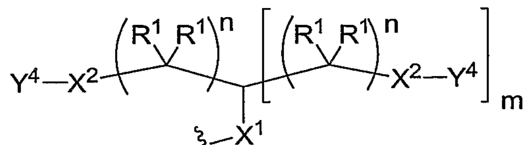
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl.

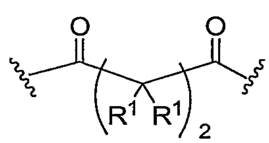
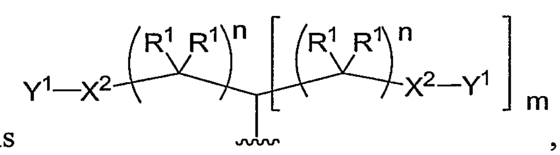
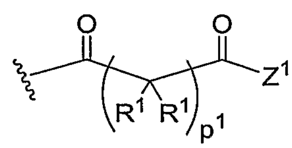
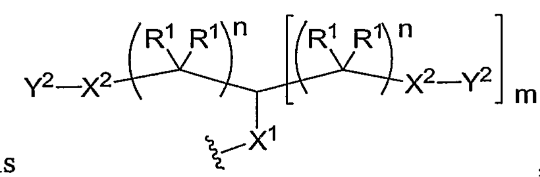
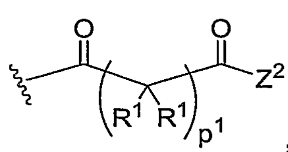
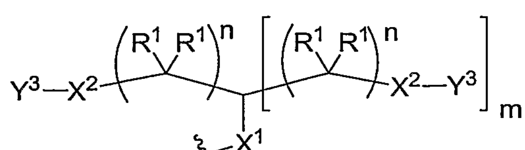
In certain instances, the present invention relates to the aforementioned method, wherein p^1 is 2, p^2 is 0, and R^3 is $(C_1\text{-}C_5)$alkyl, and w^2 is an integer in the range of about 60 to about 90.

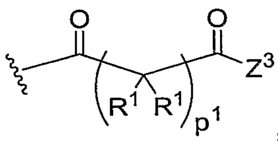
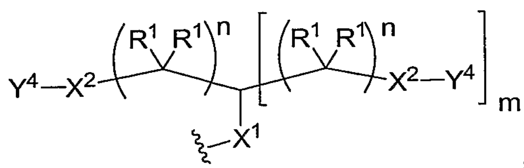
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1, or 2, Y^1 is , and Z^1 is .

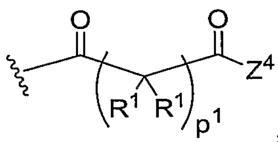
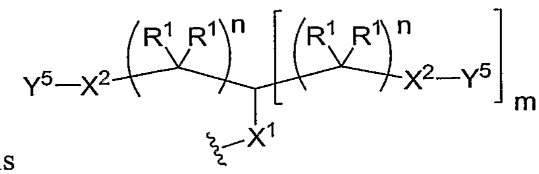
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m

is 1, or 2, Y^1 is , Z^1 is , Y^2 is , and Z^2 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1, or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is , and Z^3 is .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is H, B is , A^2 is , m is 1, or 2, Y^1 is , Z^1 is , Y^2 is , Z^2 is , Y^3 is

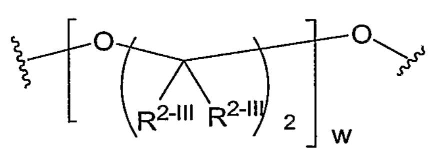
 , Z^3 is  , Y^4 is

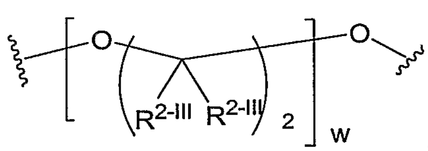
 , and Z^4 is  .

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is a compound of formula **II**.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is a compound of formula **III**.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{1\text{-III}}$ is -C(O)H, and $R^{2\text{-III}}$ is H.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{1\text{-III}}$ is -C(O)H, $R^{2\text{-III}}$ is H, and $B^{1\text{-III}}$ is  .

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **III**, $R^{2\text{-III}}$ is -C(O)H, $R^{2\text{-III}}$ is H, $B^{1\text{-III}}$ is  , and w is an integer in the range of about 100-1000.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is an oxidizing agent.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is O_2.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is ultraviolet light or visible light.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is ultraviolet light.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 400-600 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 450-550 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is light with a λ of 488-514 nm.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

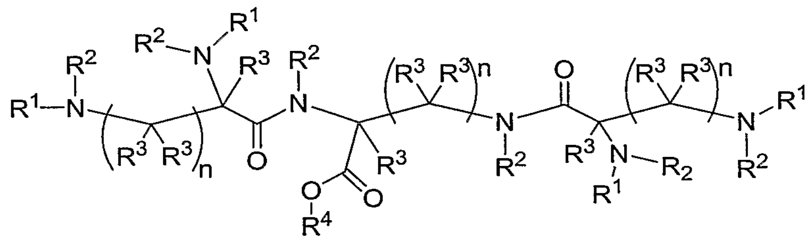
In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

In certain embodiments, the present invention relates to an ocular lens formed using the aforementioned method.

Another aspect of the present invention relates to a method of preparing an ocular lens for a patient, comprising the steps of:

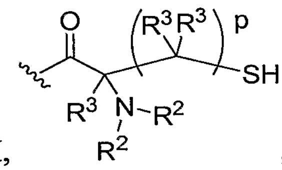
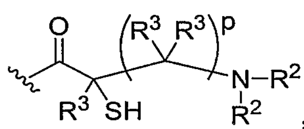
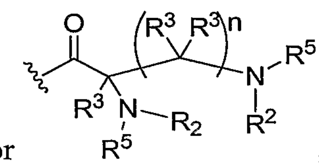
exposing a sterilized compound of formula **V** to a polymerization agent sufficient to polymerize said sterilized compound of formula **V**, wherein said polymerization agent is an oxidizing agent or compound **VI**, and formula **V** is represented by:



V

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

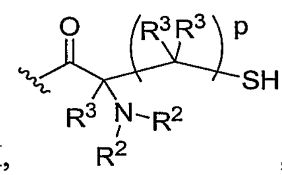
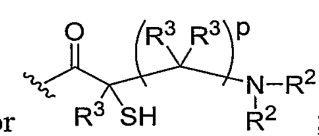
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

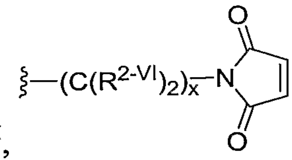
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8; and

p represents independently for each occurrence 1, 2, 3, 4, or 5; and said formula **VI** is represented by:

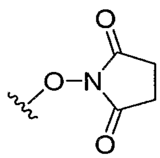
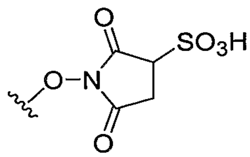
$$R^{1\text{-VI}}\text{—B—}R^{1\text{-VI}}$$

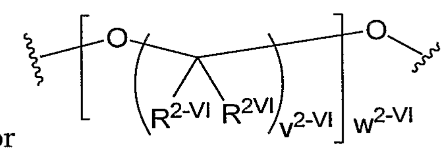
VI

wherein

R^{1-VI} represents independently for each occurrence $-(C(R^{2-VI})_2)_xC(O)H$, $-C(O)(C(R^{2-VI})_2)_yC(O)H$, $-(C(R^{2-VI})_2)_xC(O)R^{3-VI}$, $-C(O)(C(R^{2-VI})_2)_yC(O)R^{3-VI}$,  ;

R^{2-VI} represents independently for each occurrence H, alkyl, or halogen;

R^{3-VI} represents independently for each occurrence fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

B is alkyl diradical, heteroalkyl diradical, or  ;

v^{2-VI} represents independently for each occurrence 2, 3, or 4;

w^{2-VI} is an integer in the range of about 5 to 7000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is an oxidizing agent.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is O_2.

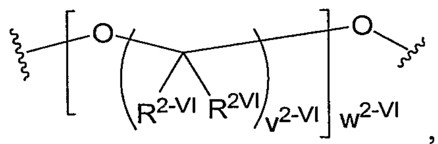
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**.

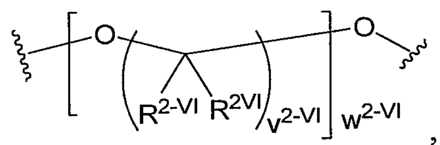
In certain instances, the present invention relates to the aforementioned method, wherein w^{2-VI} is an integer in the range of about 50 to about 250.

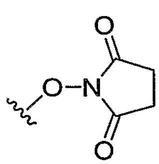
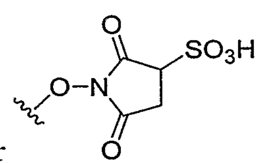
In certain instances, the present invention relates to the aforementioned method, wherein w^{2-VI} is an integer in the range of about 60 to about 90.

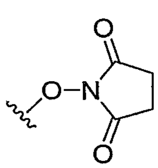
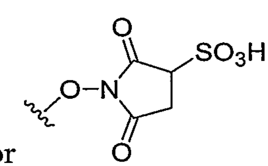
In certain instances, the present invention relates to the aforementioned method, wherein w^{2-VI} is an integer in the range of about 100 to about 1000.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, and $R^{2\text{-}VI}$ is H.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, $R^{2\text{-}VI}$ is H, B is  , and $v^{2\text{-}VI}$ is 2.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **VI**, $R^{1\text{-}VI}$ is -C(O)H, $R^{2\text{-}VI}$ is H, B is  , $v^{2\text{-}VI}$ is 2, and $w^{2\text{-}VI}$ is an integer in the range of about 60-90.

In certain instances, the present invention relates to the aforementioned method, wherein $R^{1\text{-}VI}$ is $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$ or $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, $R^{2\text{-}VI}$ is H, and $R^{3\text{-}VI}$ is  or  .

In certain instances, the present invention relates to the aforementioned method, wherein $R^{1\text{-}VI}$ is $-(C(R^{2\text{-}VI})_2)_xC(O)R^{3\text{-}VI}$ or $-C(O)(C(R^{2\text{-}VI})_2)_yC(O)R^{3\text{-}VI}$, $R^{2\text{-}VI}$ is H, $R^{3\text{-}VI}$ is  or  , $v^{2\text{-}VI}$ is 2, and $w^{2\text{-}VI}$ is an integer in the range of about 100-1000.

In certain instances, the present invention relates to the aforementioned method, wherein n is 3, 4, or 5.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4.

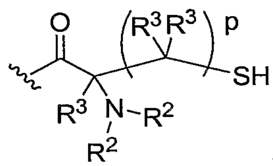
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is H.

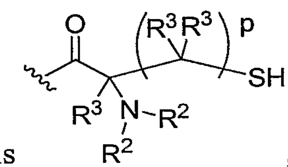
In certain instances, the present invention relates to the aforementioned method, wherein R^3 is H.

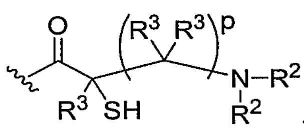
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is alkyl.

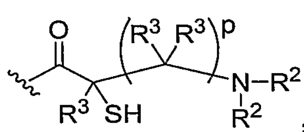
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is methyl or ethyl.

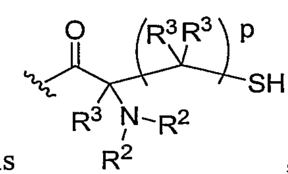
In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

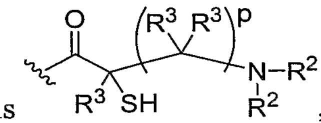
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and a Bronstead acid.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and HA, wherein A is halogen or $-O_2CR^6$, and R^6 is alkyl, fluoroalkyl, aryl, or aralkyl.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and an acid selected from group consisting of HCl and HBr.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and HO_2CR^6, wherein R^6 is fluoroalkyl.

In certain instances, the present invention relates to the aforementioned method, wherein said pharmaceutically acceptable salt is a complex formed by said compound of formula **V** and CF_3CO_2H.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

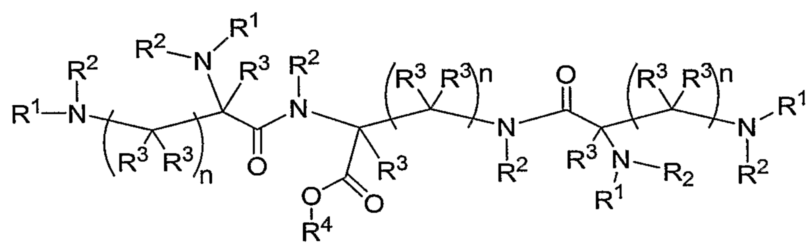
In certain embodiments, the present invention relates to the aforemention method, wherein said compound of formula **V** and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, wherein said compound of formula **V** and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

In certain embodiments, the present invention relates to an ocular lens formed using the aforementioned method.

Another aspect of the present invention relates to a method of preparing an ocular lens for a patient, comprising the steps of:

exposing a dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X** to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is an oxidizing agent or a compound of formula **XI**, and wherein formula **VII** is represented by:

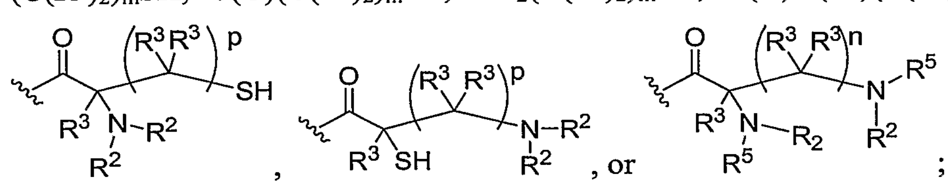


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

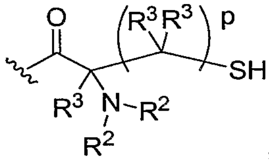


R^2 represents independently for each occurrence H or alkyl;

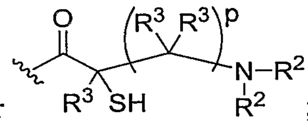
R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,



, or

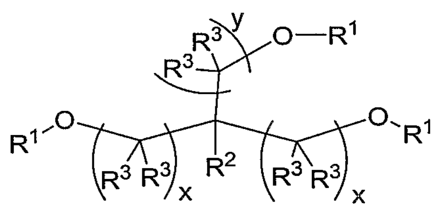


;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

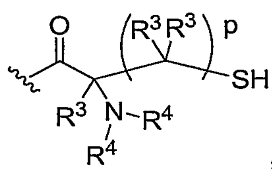
formula **VIII** is represented by:



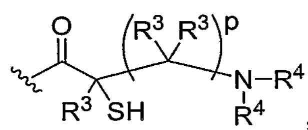
VIII

wherein

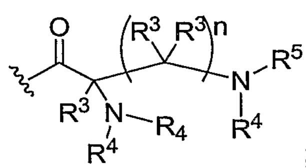
R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,



,



, or



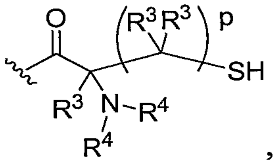
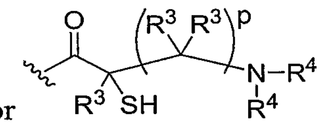
;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

, or ;

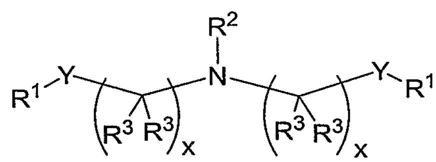
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

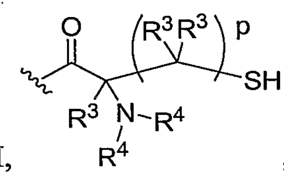
y is 0, 1, 2, 3, or 4;

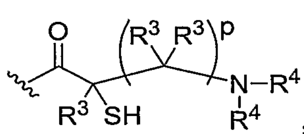
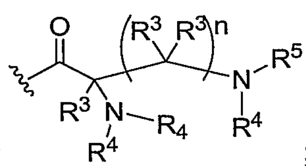
formula **IX** is represented by:



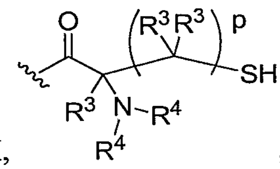
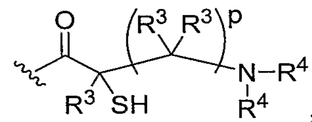
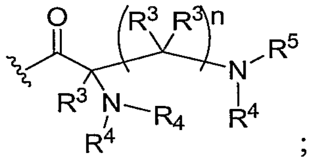
IX

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, ,

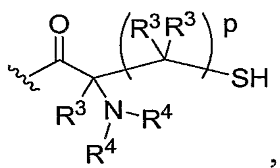
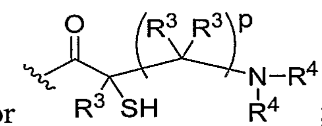
, or ;

R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, -

$CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

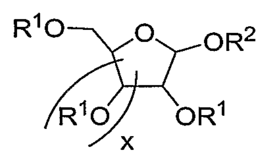
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x represents independently for each occurrence 1, 2, 3, or 4;

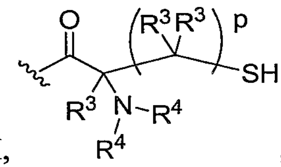
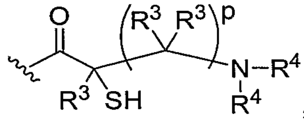
formula **X** is represented by:

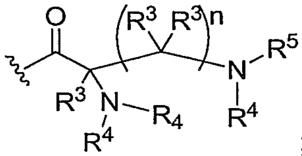


X

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$, , , or

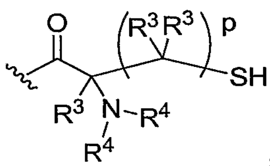
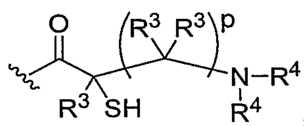
;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

, or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2; and

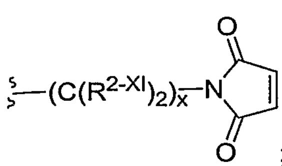
formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

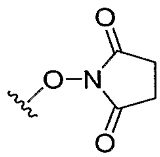
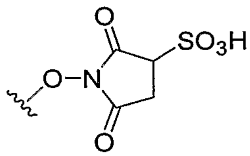
XI

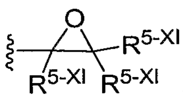
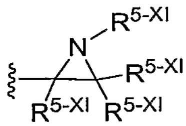
wherein

$R^{1\text{-}XI}$ represents independently for each occurrence $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yR^{4\text{-}XI}$, or

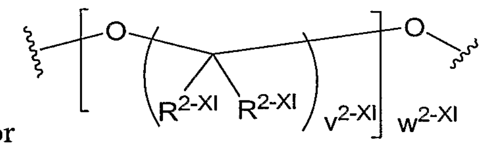
;

$R^{2\text{-}XI}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}XI}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2,  , or  ;

$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S,  , or  ;

$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or  ;

$v^{2\text{-}XI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}XI}$ is an integer in the range of about 5 to 7000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is an oxidizing agent.

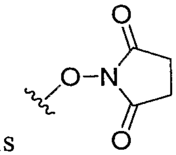
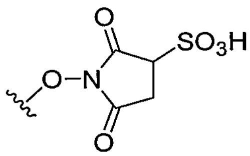
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is O_2.

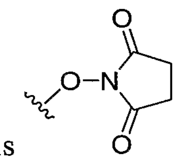
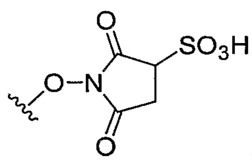
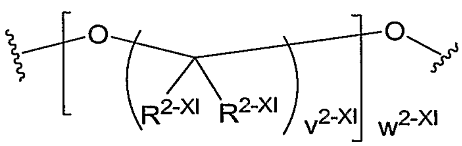
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**.

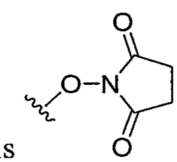
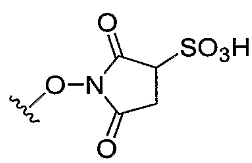
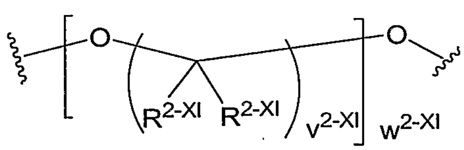
In certain instances, the present invention relates to the aforementioned method, wherein $w^{2\text{-}XI}$ is an integer in the range of about 100 to about 1000.

In certain instances, the present invention relates to the aforementioned method, wherein $w^{2\text{-}XI}$ is an integer in the range of about 60 to about 90.

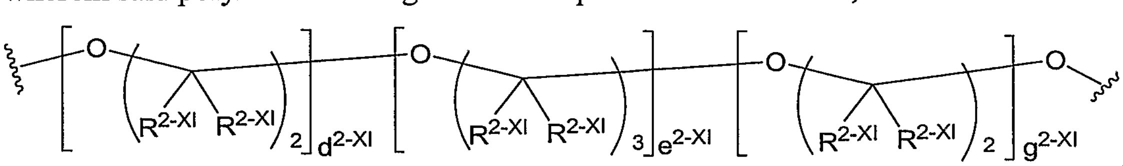
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, $R^{1\text{-}XI}$ is -(C($R^{2\text{-}}$

${}^{XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is  or  .

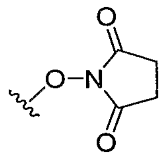
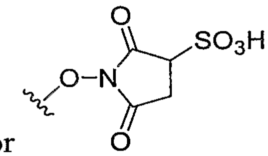
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or  , B is  , and $v^{2\text{-}XI}$ is 2.

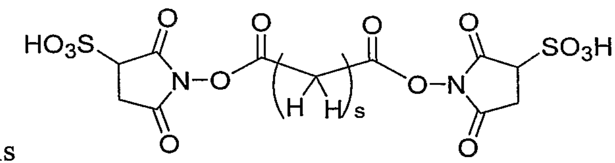
In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or  , B is  , $v^{2\text{-}VII}$ is 2, and $w^{2\text{-}XI}$ is an integer in the range of about 100-1000.

In certain instances, the present invention relates to the aforementioned method, wherein said polymerization agent is a compound of formula **XI**, wherein B is



, and $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ represent independently an integer greater than zero, provided that the sum of $d^{2\text{-}XI}$, $e^{2\text{-}XI}$, and $g^{2\text{-}XI}$ is an integer in the range of about 5 to 7000, inclusive.

In certain instances, the present invention relates to the aforementioned method, wherein, RR^{1-XI} is $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$ or $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, R^{2-XI} is H, and R^{3-XI} is  or  .

In certain instances, the present invention relates to the aforementioned method, wherein, formula **XI** is  , and s is an integer in the range of about 1-20, inclusive.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VII**.

In certain instances, the present invention relates to the aforementioned method, wherein n is 3, 4, or 5.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4.

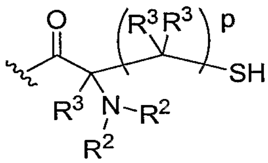
In certain instances, the present invention relates to the aforementioned method, wherein R^2 is H.

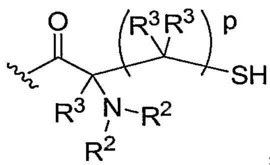
In certain instances, the present invention relates to the aforementioned method, wherein R^3 is H.

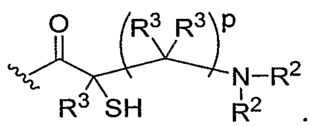
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is alkyl.

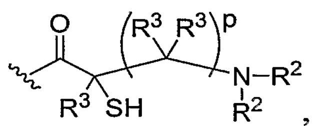
In certain instances, the present invention relates to the aforementioned method, wherein R^4 is methyl or ethyl.

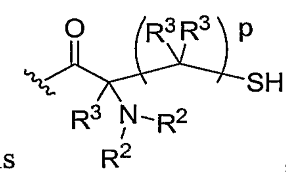
In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

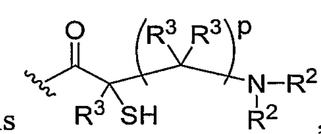
In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  .

In certain instances, the present invention relates to the aforementioned method, wherein R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is  , and p is 1.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**, x and y are 1, R^2 is -CH_2OR^1, and R^3 is H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **VIII**, x is 1, y is 0, and R^2 and R^3 are H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is O, R^2 is $-CH_2CH_2OR^1$, and R^3 is H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is NR^4, and R^2 and R^3 are H.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **X**.

In certain instances, the present invention relates to the aforementioned method, wherein said dendrimeric compound is a compound of formula **X**, R^2 is methyl, and x is 2.

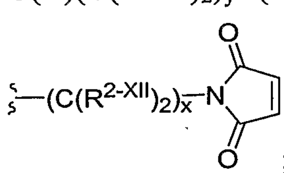
In certain instances, the present invention relates to the aforementioned method, further comprising the step of exposing said dendrimeric compound to a compound of formula **XII**, wherein formula **XII** is represented by:

$$R^{1\text{-}XII}—B^{XII}—R^{1\text{-}XII}$$

XII

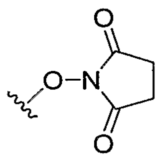
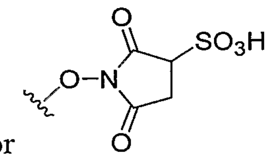
wherein

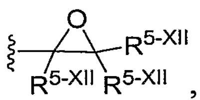
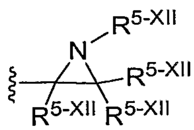
$R^{1\text{-}XII}$ represents independently for each occurrence $-(C(R^{2\text{-}XII})_2)_xC(O)R^{3\text{-}XII}$, $-C(O)(C(R^{2\text{-}XII})_2)_yC(O)R^{3\text{-}XII}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XII}$, $-C(O)(C(R^{2\text{-}XII})_2)_yR^{4\text{-}XII}$, or



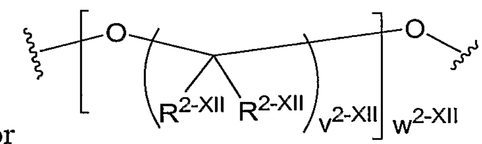
;

$R^{2\text{-}XII}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-XII}}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2, , or ;

$R^{4\text{-XI}}$ represents independently for each occurrence -N=C=O, -N=C=S, , or ;

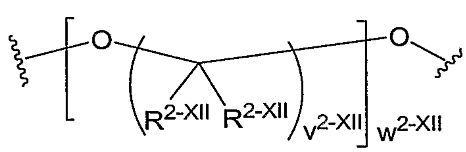
$R^{5\text{-XI}}$ represents independently for each occurrence H, alkyl, or aralkyl;

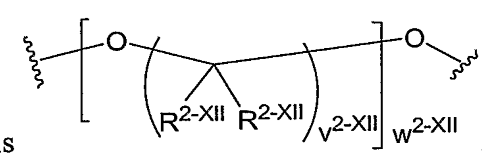
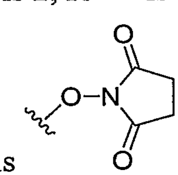
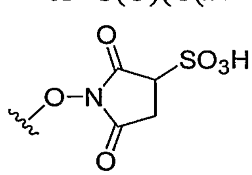
B^{XII} is alkyl diradical, heteroalkyl diradical, or ;

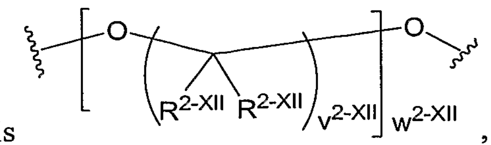
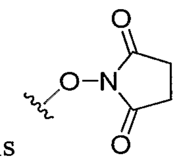
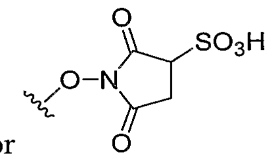
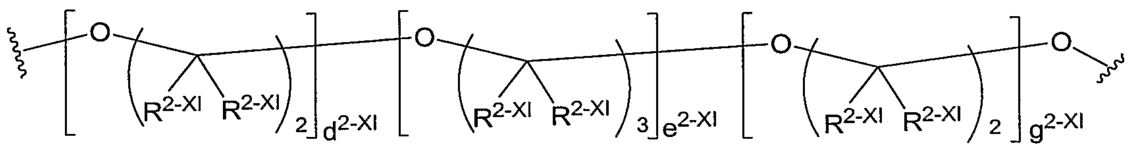
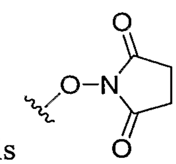
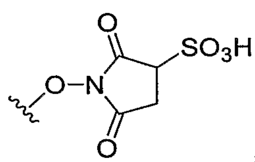
$v^{2\text{-XII}}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-XII}}$ is an integer in the range of about 5 to 7000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is , and $v^{2\text{-XII}}$ is 2.

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is , $v^{2\text{-XII}}$ is 2, $R^{1\text{-XII}}$ is $-(C(R^{2\text{-XII}})_2)_xC(O)R^{3\text{-XII}}$ or $-C(O)(C(R^{2\text{-XII}})_2)_yC(O)R^{3\text{-XII}}$, $R^{2\text{-XII}}$ is H, and $R^{3\text{-XII}}$ is  or .

In certain embodiments, the present invention relates to the aforemention method, wherein, B^{XII} is , v^{2-XII} is 2, R^{1-XII} is $-(C(R^{2-XII})_2)_xC(O)R^{3-XII}$ or $-C(O)(C(R^{2-XII})_2)_yC(O)R^{3-XII}$, R^{2-XII} is H, R^{3-XII} is  or , said polymerization agent is a compound of formula **XI**, B is , R^{1-XI} is $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$ or $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, R^{2-XI} is H, R^{3-XI} is  or , and d^{2-XI}, e^{2-XI}, and g^{2-XI} represent independently an integer greater than zero, provided that the sum of d^{2-XI}, e^{2-XI}, and g^{2-XI} is an integer in the range of about 5 to 7000, inclusive.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a primate, bovine, equine, feline, or canine.

In certain embodiments, the present invention relates to the aforemention method, wherein said patient is a human.

In certain embodiments, the present invention relates to the aforemention method, further comprising the step of sterilizing said dendrimeric compound.

In certain embodiments, the present invention relates to the aforemention method, further comprising the step of sterilizing said polymerization agent, wherein said polymerization agent is a compound of formula **XI**.

In certain embodiments, the present invention relates to the aforemention method, further comprising the step of sterilizing said dendrimeric compound and said polymerization agent, wherein said polymerization agent is a compound of formula **XI**.

In certain embodiments, the present invention relates to the aforemention method, wherein said sterilizing is performed by treatment with ethylene oxide, hydrogen peroxide, heat, gamma irradiation, electron beam irradiation, microwave irradiation, or visible light irradiation.

In certain embodiments, the present invention relates to the aforemention method, wherein said sterilizing is effective to achieve a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned method, wherein said sterilizing is effective to achieve a sterility assurance level of at least about 10^{-6}.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said polymerization agent is sterile.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforemention method, wherein said dendrimeric compound and said polymerization agent have a sterility assurance level of at least about 10^{-6}.

In certain embodiments, the present invention relates to an ocular lens formed using the aforementioned method.

Compositions & Methods of Treatment of the Invention

One aspect of the invention relates to the polymeric composition formed by exposing a dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X** to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is an oxidizing agent or a compound of formula **XI**, and wherein formulae **VII**, **VIII**, **IX**, **X**, and **XI** are as defined above.

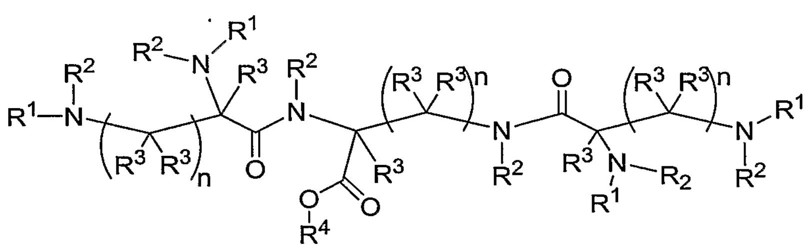
Another aspect of the invention relates to the polymeric composition formed by exposing a dendrimeric compound of formulae **VII, VIII, IX,** or **X** to a polymerization agent and a compound of formula **XII** sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is a compound of formula **XI**, and wherein formulae **VII, VIII, IX, X, XI**, and **XII** are as defined above.

Another aspect of the invention relates to a polymeric composition represented by formula **XIII**:

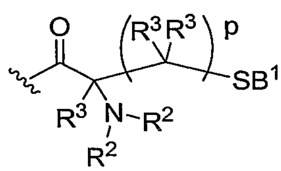
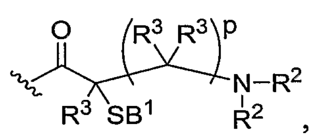
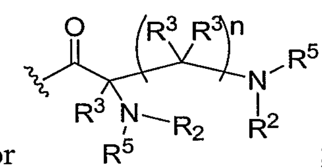
$$A^1\left[L^1-A^2\left[L^2-A^3\right]_d\right]_e$$

XIII

wherein

A^1 is  or a pharmaceutically acceptable salt, solvate, or hydrate thereof;

R^1 represents independently for each occurrence H, $-OB^1$, $-(C(R^3)_2)_mN(R^2)OB^1$, $-(C(R^3)_2)_mSB^1$, $-C(O)(C(R^3)_2)_mSB^1$, $-CO_2(C(R^3)_2)_mSB^1$, $-C(O)N(R^2)(C(R^3)_2)_mSB^1$,

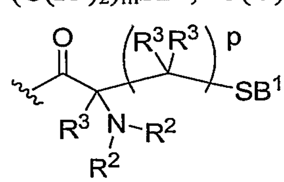
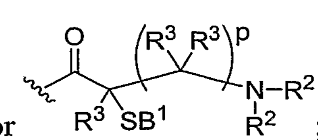
 ,  , or  ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence $-OB^1$, $-(C(R^3)_2)_mN(R^2)OB^1$, $-(C(R^3)_2)_mSB^1$, $-C(O)(C(R^3)_2)_mSB^1$, $-CO_2(C(R^3)_2)_mSB^1$, $-C(O)N(R^2)(C(R^3)_2)_mSB^1$,

 , or  ;

B^1 represents independently for each occurrence H or a bond to L^1;

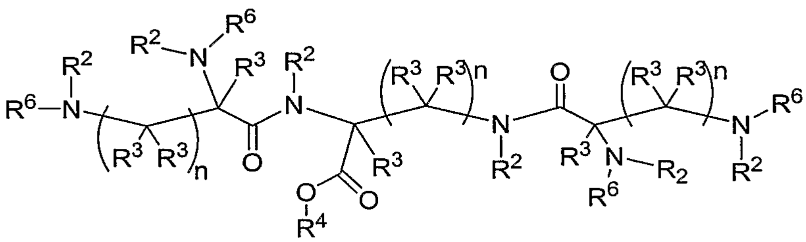
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

d represents independently for each occurrence 0, 1, or 2;

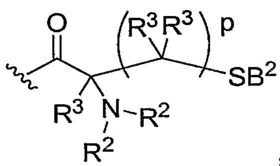
e is 1, 2, 3, or 4;

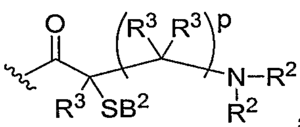
A^2 represents independently for each occurrence

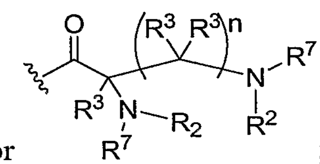


or a pharmaceutically acceptable salt, solvate, or hydrate thereof;

R^6 represents independently for each occurrence H, $-OB^2$, $-(C(R^3)_2)_mN(R^2)OB^2$, $-(C(R^3)_2)_mSB^2$, $-C(O)(C(R^3)_2)_mSB^2$, $-CO_2(C(R^3)_2)_mSB^2$, $-C(O)N(R^2)(C(R^3)_2)_mSB^2$,

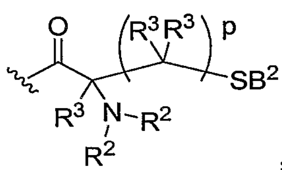


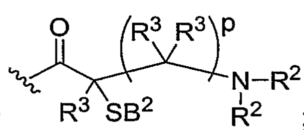
, 

, or 

;

R^7 represents independently for each occurrence $-OB^2$, $-(C(R^3)_2)_mN(R^2)OB^2$, $-(C(R^3)_2)_mSB^2$, $-C(O)(C(R^3)_2)_mSB^2$, $-CO_2(C(R^3)_2)_mSB^2$, $-C(O)N(R^2)(C(R^3)_2)_mSB^2$,

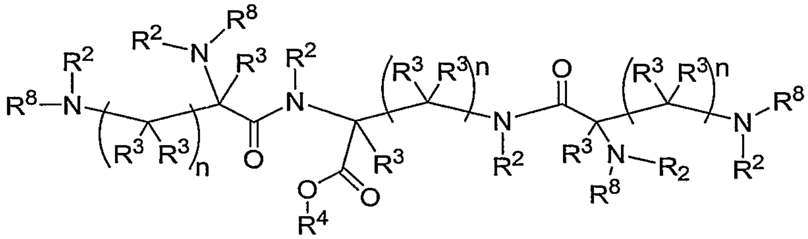


, or 

;

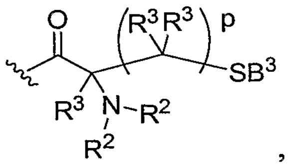
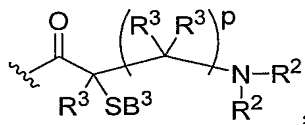
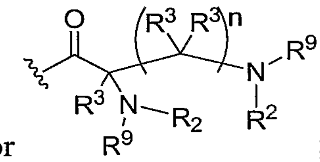
B^2 represents independently for each occurrence H, a bond to L^1, or a bond to L^2;

A^3 represents independently for each occurrence

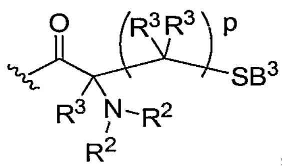
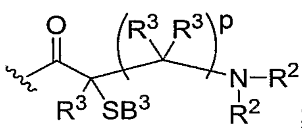


or a pharmaceutically acceptable salt, solvate, or hydrate thereof;

R^8 represents independently for each occurrence H, $-OB^3$, $-(C(R^3)_2)_mN(R^2)OB^3$, $-(C(R^3)_2)_mSB^3$, $-C(O)(C(R^3)_2)_mSB^3$, $-CO_2(C(R^3)_2)_mSB^3$, $-C(O)N(R^2)(C(R^3)_2)_mSB^3$,

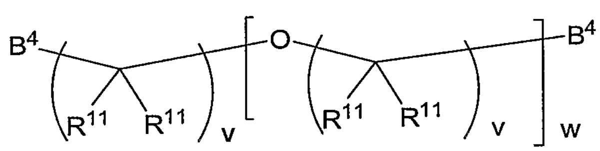
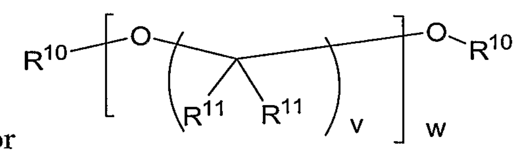
 ,  , or  ;

R^9 represents independently for each occurrence $-OB^3$, $-(C(R^3)_2)_mN(R^2)OB^3$, $-(C(R^3)_2)_mSB^3$, $-C(O)(C(R^3)_2)_mSB^3$, $-CO_2(C(R^3)_2)_mSB^3$, $-C(O)N(R^2)(C(R^3)_2)_mSB^3$,

 , or  ;

B^3 represents independently for each occurrence H or a bond to L^2;

L^1 represents independently for each occurrence

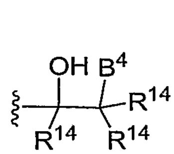
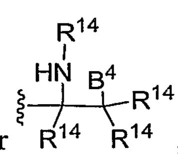
 or  ;

R^{10} represents independently for each occurrence $-(C(R^{11})_2)_xC(O)B^4$, $-(C(R^{11})_2)_xR^{12}$, $-C(O)(C(R^{11})_2)_yC(O)B^4$, $-C(O)(C(R^{11})_2)_yR^{12}$, $-(C(R^{11})_2)_xR^{13}$, or $-C(O)(C(R^{11})_2)_yR^{13}$;

R^{11} represents independently for each occurrence H, alkyl, or halogen;

R^{12} represents independently for each occurrence $-C(OH)(alkyl)B^4$, $-C(OH)(fluoroalkyl)B^4$, $-C(OH)(chloroalkyl)B^4$, or $-C(OH)(CH_2NO_2)B^4$;

R^{13} represents independently for each occurrence $-N(H)C(O)B^4$, $-N(H)C(S)B^4$,

 , or  ;

R^{14} represents independently for each occurrence H, alkyl, or aralkyl;

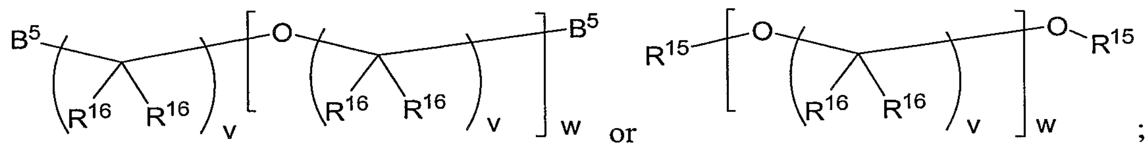
B^4 represents independently for each occurrence a bond to A^1 or A^2;

v represents independently for each occurrence 2, 3, or 4;

w is an integer in the range of about 5 to 7000, inclusive;

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9;

L^2 represents independently for each occurrence

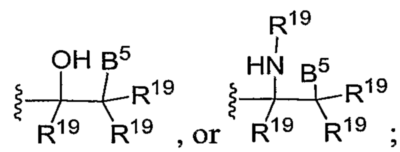


R^{15} represents independently for each occurrence $-(C(R^{16})_2)_xC(O)B^5$, $-(C(R^{16})_2)_xR^{17}$, $-C(O)(C(R^{16})_2)_yC(O)B^5$, $-C(O)(C(R^{16})_2)_yR^{17}$, $-(C(R^{16})_2)_xR^{18}$, or $-C(O)(C(R^{16})_2)_yR^{18}$;

R^{16} represents independently for each occurrence H, alkyl, or halogen;

R^{17} represents independently for each occurrence $-C(OH)(alkyl)B^5$, $-C(OH)(fluoroalkyl)B^5$, $-C(OH)(chloroalkyl)B^5$, or $-C(OH)(CH_2NO_2)B^5$;

R^{18} represents independently for each occurrence $-N(H)C(O)B^5$, $-N(H)C(S)B^5$,



R^{19} represents independently for each occurrence H, alkyl, or aralkyl; and

B^5 represents independently for each occurrence a bond to A^2 or A^3.

In certain embodiments, the present invention relates to the aforementioned composition, wherein w is an integer in the range of about 5 to 700, inclusive.

Another aspect of the invention relates to a pharmaceutical composition comprising the above polymeric composition and a pharmaceutical agent.

In certain embodiments, the present invention relates to the aforementioned composition, wherein said pharmaceutical agent is 10-hydroxycamptothecin, diclofenac, ibuprofen, ketoprofen, naproxen, codeine, fentanyl, hydromorphone, morphine, cimetidine, famotidine, nizadine, ranitidine, amphotericin b, clotrimazole, fluconazole, ketoconazole, doxycycline, minocycline, tetracycline, aldesleukin, interleukin-2, docetaxel, etoposide, interferon alfa, paclitaxel, tretinoin, bleomycin, dactinomycin, daunorubicin, doxorubicin, mitomycin, atropine, oxybutynin, nifedipine, verapamil, idocaine, mexiletine, phenytoin, procainamide, quinidine, atenolol, metoprolol, propranolol, timolol, amphotericin B, clotrimazole, miconazole, nystatin, erythropoietin, filgrastim, desmopressin, goserelin, oxytocin, beclomethasone, betamethasone, cortisone, dexamethasone, hydrocortisone,

prednisone, diclofenac, ibuprofen, ketoprofen, ketorlac, naproxen, flurbiprofen, ivermectin, levodopa, nafarelin, or somatropin.

Another aspect of the invention relates to a method of treating a mammal suffering from cancer, depression, inflammation, cardiovascular disease, insomnia, bacterial infection, viral infection, fungal infection, malaria, parkinson's disease, pain, hypertension, organ transplant or skin graft rejection, allergies, inflammation brain cell destruction, excess gastric secretion, diarrhoea, respiratory disease, cough and respiratory depression, obesity, depression, bipolar disorders, anxiety disorders, obsessive-compulsive disorders, social phobias or panic states, sleep disorder, sexual dysfunction, psychoses, schizophrenia, migraine and other conditions associated with cephalic pain or other pain, epilepsy, personality disorders, age-related behavioural disorders, behavioural disorders associated with dementia, aggressivity, age-related memory disorder, chronic fatigue syndrome, drug and alcohol addiction, bulimia, anorexia nervosa, or premenstrual tension, comprising the step of:

administering to said mammal a therapeutically effective amount of any one of the pharmaceutical compositions described herein.

In certain embodiments, the present invention relates to the aforementioned method, wherein said disease is cancer, and said pharmaceutical agent is an anti-cancer agent.

In certain embodiments, the present invention relates to the aforementioned method, wherein said pharmaceutical agent is 10-hydroxycamptothecin.

Kits of the Invention

One aspect of the present invention relates to a kit for the preparation of a sealant comprising:

a polymerizable dendrimeric compound of formula **I**, wherein formula **I** is as defined above; and

instructions for preparing said sealant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a desiccant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a polymerization agent.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said polymerization agent is a compound of formula **II**, a compound of formula **III**, or a compound of formula **IV**; wherein formulae **II**, **III**, and **IV** are as defined above.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a kit for the preparation of a sealant comprising:

a polymerizable dendrimeric compound of formula **V**, wherein formula **V** is as defined above; and

instructions for preparing said sealant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a desiccant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a polymerization agent.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said polymerization agent is a compound of formula **VI**; wherein formula **VI** is as defined above.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a kit for the preparation of a sealant comprising:

a polymerizable dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X**, wherein formulae **VII**, **VIII**, **IX**, and **X** are as defined above; and

instructions for preparing said sealant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a desiccant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a polymerization agent.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said polymerization agent is a compound of formula **XI**; wherein formula **XI** is as defined above.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a compound of formula **XII**.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a kit for the preparation of a lens comprising:

a polymerizable dendrimeric compound of formula **I**, wherein formula **I** is as defined above; and

instructions for preparing said lens.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a desiccant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a polymerization agent.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said polymerization agent is a compound of formula **II**, a compound of formula **III**, or a compound of formula **IV**; wherein formulae **II**, **III**, and **IV** are as defined above.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a kit for the preparation of a lens comprising:

a polymerizable dendrimeric compound of formula **V**, wherein formula **V** is as defined above; and

instructions for preparing said lens.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a desiccant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a polymerization agent.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said polymerization agent is a compound of formula **VI**; wherein formula **VI** is as defined above.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Another aspect of the present invention relates to a kit for the preparation of a lens comprising:

a polymerizable dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X**, wherein formulae **VII**, **VIII**, **IX**, and **X** are as defined above; and

instructions for preparing said lens.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a desiccant.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a polymerization agent.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said polymerization agent is a compound of formula **XI**; wherein formula **XI** is as defined above.

In certain embodiments, the present invention relates to the aforementioned kit, further comprising a compound of formula **XII**.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-3}.

In certain embodiments, the present invention relates to the aforementioned kit, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Devices and Methods for Controlling Polymerization of the Invention

One aspect of the invention relates to a method of controlling the polymerization of a hydrogel system, comprising the steps of:

admixing hydrogel-forming components to form a first solution with a pH unsuitable for crosslinking, and contacting said first solution with an ion exchange resin to produce a second solution having a pH suitable for crosslinking.

In certain embodiments, the present invention relates to the aforementioned method, wherein said hydrogel-forming components are PEG-SPA and Lys3Cys4, the pH of said first solution is less than about 7, and the ion exchange resin is an anion exchange resin.

In certain embodiments, the present invention relates to the aforementioned method, wherein said anion exchange resin is MTO-Dowex M43, Dowex 66, or Dowex 1X2-200.

In certain embodiments, the present invention relates to the aforementioned method, wherein the pH of said second solution is greater than about 7.2.

Another aspect of the invention relates to a method of controlling the polymerization of a hydrogel system, comprising the steps of:

admixing hydrogel-forming components to form a first solution with a pH unsuitable for crosslinking, and contacting said first solution with an acidic resin to produce a second solution having a pH suitable for crosslinking.

Another aspect of the invention relates to a method of controlling the polymerization of a hydrogel system, comprising the steps of:

admixing hydrogel-forming components to form a first solution with a pH unsuitable for crosslinking, and contacting said first solution with a basic resin to produce a second solution having a pH suitable for crosslinking.

In certain embodiments, the present invention relates to the aforementioned method, wherein said resin comprises sodium carbonate or sodium phosphate dibasic.

In certain embodiments, the present invention relates to the aforementioned method, wherein said hydrogel-forming components are PEG-SPA and Lys3Cys4.

Another aspect of the present invention relates to a delivery device comprising a first compartment containing a nucleophilic compound and an electrophilic compound used to form a hydrogel, a second compartment containing a buffered solution with a pH outside of the range for effective crosslinking, a breakable seal separating the first and second compartments, and a third compartment that surrounds the first and second compartments and contains a resin.

In certain embodiments, the present invention relates to the aforementioned device, wherein said seal is a thin layer of glass.

In certain embodiments, the present invention relates to the aforementioned device, wherein said resin is an anionic ion exchange resin.

In certain embodiments, the present invention relates to the aforementioned device, further comprising a hydrophobic permeable layer separating the first and second compartments from the resin.

Definitions

For convenience, certain terms employed in the specification, examples, and appended claims are collected here.

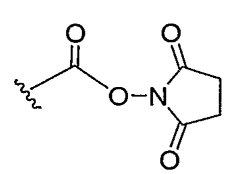
The term "generation" refers to the number of branched repeat units which emanate from the central core. For example a third generation (or G3) PGLSA dendrimer has three branching layers not including the core.

The term "polymerize" as used herein refers to the process of converting a monomer to a chain of momomers, wherein the chain of momomers comprises at least about 5 monomers. In certain instances, the chain of monomers comprises at least about 10 or 15 momomers. In certain instances, the chain of monomers comprises at least about 25 or 40 momomers. In certain instances, the chain of monomers comprises at least about 50 or 75 momomers. In certain instances, the chain of monomers comprises at least about 100 or 150 momomers. In instances wherein the monomeric unit has more than one functional group capable of forming a bond in the polymerization reaction, the term "polymerize" indicates that at least one of functional groups capable of forming a bond in the polymerization reaction forms a bond with another compound, generally speaking, the other compound is another monomer. In certain instances, at least about 10% of the functional

groups capable of forming a bond in a polymerization reaction form a bond to another monomer. In certain instances, at least about 25% of the functional groups capable of forming a bond in a polymerization reaction form a bond to another monomer. In certain instances, at least about 50% of the functional groups capable of forming a bond in a polymerization reaction form a bond to another monomer. In certain instances, at least about 75% of the functional groups capable of forming a bond in a polymerization reaction form a bond to another monomer. In certain instances, about 20% to about 50% of the functional groups capable of forming a bond in a polymerization reaction form a bond to another monomer.

The term "seal" as used herein indicates that a protective barrier is formed over the wound. In certain instances, the protective barrier is a continuous layer. In certain instances, the protective barrier is a discontinous layer, i.e., a layer that has holes or pores in the layer. In certain instances, the discontinous layer comprises less than about 25% holes. In certain instances, the discontinous layer comprises about less than 15% holes. In certain instances, the discontinous layer comprises about less than 5% holes. In the instance where the protective barrier is a continuous layer, certain fluids or gases can penetrate through the layer. In certain instances, the fluid is a liquid located in the eye. In certain instances, the fluid is water. In instances when the wound is an ophthalmic wound, the seal prevents fluid from exiting the wound when the pressure in the eye is less than about 40 mm Hg. In certain instances, the seal prevents fluid from exiting the wound when the pressure in the eye is less than about 60 mm Hg. In certain instances, the seal prevents fluid from exiting the wound when the pressure in the eye is less than about 80 mm Hg. In certain instances, the seal prevents fluid from exiting the wound when the pressure in the eye is less than about 100 mm Hg. In certain instances, the seal prevents fluid from exiting the wound when the pressure in the eye is less than about 120 or about 150 mm Hg. In certain instances, the seal prevents fluid from exiting the wound when the pressure in the eye is less than about 180 or about 200 mm Hg.

The term "PEG(NHS)$_2$" refers to a polyethylene glycol having the following functional group attached at both ends of the polymer chain:



$PEG(NHS)_2$ can be prepared using either of the following methods. In method 1, a polyethylene glycol is subjected to oxidative conditions in order to oxidize the two termini to the corresponding carboxylic acids [HO_2CCH_2O-PEG-OCH_2CO_2H], followed by transformation to the bis(NHS ester). In method 2, $PEG(NHS)_2$ is prepared by alkylation of the two termini of a polyethylene glycol with acrylonitrile to give $NCCH_2CH_2O$-PEG-OCH_2CH_2CN, followed by hydrolysis to the bis(acid) [$HO_2CCH_2CH_2O$-PEG-$OCH_2CH_2CO_2H$], and then transformation to the bis(NHS ester).

The term "heteroatom" as used herein means an atom of any element other than carbon or hydrogen. Preferred heteroatoms are boron, nitrogen, oxygen, phosphorus, sulfur and selenium.

The term "alkyl" refers to the radical of saturated aliphatic groups, including straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl substituted cycloalkyl groups, and cycloalkyl substituted alkyl groups. In preferred embodiments, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., C_1-C_{30} for straight chain, C_3-C_{30} for branched chain), and more preferably 20 or fewer. Likewise, preferred cycloalkyls have from 3-10 carbon atoms in their ring structure, and more preferably have 5, 6 or 7 carbons in the ring structure.

Unless the number of carbons is otherwise specified, "lower alkyl" as used herein means an alkyl group, as defined above, but having from one to ten carbons, more preferably from one to six carbon atoms in its backbone structure. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths. Preferred alkyl groups are lower alkyls. In preferred embodiments, a substituent designated herein as alkyl is a lower alkyl.

The term "aralkyl", as used herein, refers to an alkyl group substituted with an aryl group (e.g., an aromatic or heteroaromatic group).

The terms "alkenyl" and "alkynyl" refer to unsaturated aliphatic groups analogous in length and possible substitution to the alkyls described above, but that contain at least one double or triple bond respectively.

The term "aryl" as used herein includes 5-, 6- and 7-membered single-ring aromatic groups that may include from zero to four heteroatoms, for example, benzene, anthracene, naphthalene, pyrene, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine, and the like. Those aryl groups having heteroatoms in the ring structure may also be referred to as "aryl heterocycles" or

"heteroaromatics." The aromatic ring can be substituted at one or more ring positions with such substituents as described above, for example, halogen, azide, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, alkoxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, sulfonamido, ketone, aldehyde, ester, heterocyclyl, aromatic or heteroaromatic moieties, $-CF_3$, -CN, or the like. The term "aryl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings (the rings are "fused rings") wherein at least one of the rings is aromatic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls.

The terms *ortho*, *meta* and *para* apply to 1,2-, 1,3- and 1,4-disubstituted benzenes, respectively. For example, the names 1,2-dimethylbenzene and *ortho*-dimethylbenzene are synonymous.

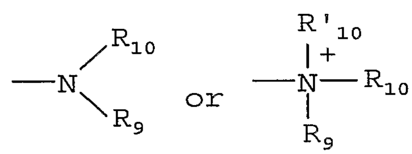
The terms "heterocyclyl" or "heterocyclic group" refer to 3- to 10-membered ring structures, more preferably 3- to 7-membered rings, whose ring structures include one to four heteroatoms. Heterocycles can also be polycycles. Heterocyclyl groups include, for example, thiophene, thianthrene, furan, pyran, isobenzofuran, chromene, xanthene, phenoxathiin, pyrrole, imidazole, pyrazole, isothiazole, isoxazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, indazole, purine, quinolizine, isoquinoline, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, carbazole, carboline, phenanthridine, acridine, pyrimidine, phenanthroline, phenazine, phenarsazine, phenothiazine, furazan, phenoxazine, pyrrolidine, oxolane, thiolane, oxazole, piperidine, piperazine, morpholine, lactones, lactams such as azetidinones and pyrrolidinones, sultams, sultones, and the like. The heterocyclic ring can be substituted at one or more positions with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, $-CF_3$, -CN, or the like.

The terms "polycyclyl" or "polycyclic group" refer to two or more rings (e.g., cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocyclyls) in which two or more carbons are common to two adjoining rings, e.g., the rings are "fused rings". Rings that are joined through non-adjacent atoms are termed "bridged" rings. Each of the rings of the

polycycle can be substituted with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphonate, phosphinate, carbonyl, carboxyl, silyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, -CF_3, -CN, or the like.

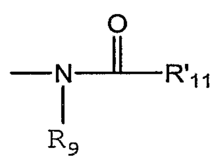
As used herein, the term "nitro" means -NO_2; the term "halogen" designates -F, -Cl, -Br or -I; the term "sulfhydryl" means -SH; the term "hydroxyl" means -OH; and the term "sulfonyl" means -SO_2-.

The terms “amine” and “amino” are art-recognized and refer to both unsubstituted and substituted amines, e.g., a moiety that can be represented by the general formula:



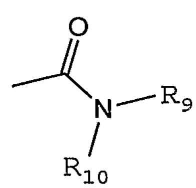
wherein R_9, R_{10} and R'_{10} each independently represent a group permitted by the rules of valence.

The term "acylamino" is art-recognized and refers to a moiety that can be represented by the general formula:



wherein R_9 is as defined above, and R'_{11} represents a hydrogen, an alkyl, an alkenyl or -$(CH_2)_m$-R_8, where m and R_8 are as defined above.

The term "amido" is art recognized as an amino-substituted carbonyl and includes a moiety that can be represented by the general formula:

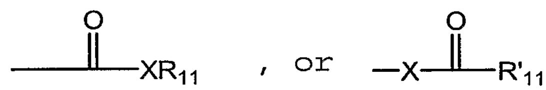


wherein R_9, R_{10} are as defined above. Preferred embodiments of the amide will not include imides which may be unstable.

The term "alkylthio" refers to an alkyl group, as defined above, having a sulfur radical attached thereto. In preferred embodiments, the "alkylthio" moiety is represented by

one of -S-alkyl, -S-alkenyl, -S-alkynyl, and -S-$(CH_2)_m$-R_8, wherein m and R_8 are defined above. Representative alkylthio groups include methylthio, ethyl thio, and the like.

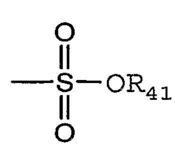
The term "carbonyl" is art recognized and includes such moieties as can be represented by the general formula:



wherein X is a bond or represents an oxygen or a sulfur, and R_{11} represents a hydrogen, an alkyl, an alkenyl, -$(CH_2)_m$-R_8 or a pharmaceutically acceptable salt, R'_{11} represents a hydrogen, an alkyl, an alkenyl or -$(CH_2)_m$-R_8, where m and R_8 are as defined above. Where X is an oxygen and R_{11} or R'_{11} is not hydrogen, the formula represents an "ester". Where X is an oxygen, and R_{11} is as defined above, the moiety is referred to herein as a carboxyl group, and particularly when R_{11} is a hydrogen, the formula represents a "carboxylic acid". Where X is an oxygen, and R'_{11} is hydrogen, the formula represents a "formate". In general, where the oxygen atom of the above formula is replaced by sulfur, the formula represents a "thiolcarbonyl" group. Where X is a sulfur and R_{11} or R'_{11} is not hydrogen, the formula represents a "thiolester." Where X is a sulfur and R_{11} is hydrogen, the formula represents a "thiolcarboxylic acid." Where X is a sulfur and R_{11}' is hydrogen, the formula represents a "thiolformate." On the other hand, where X is a bond, and R_{11} is not hydrogen, the above formula represents a "ketone" group. Where X is a bond, and R_{11} is hydrogen, the above formula represents an "aldehyde" group.

The terms "alkoxyl" or "alkoxy" as used herein refers to an alkyl group, as defined above, having an oxygen radical attached thereto. Representative alkoxyl groups include methoxy, ethoxy, propyloxy, tert-butoxy and the like. An "ether" is two hydrocarbons covalently linked by an oxygen. Accordingly, the substituent of an alkyl that renders that alkyl an ether is or resembles an alkoxyl, such as can be represented by one of -O-alkyl, -O-alkenyl, -O-alkynyl, -O-$(CH_2)_m$-R_8, where m and R_8 are described above.

The term "sulfonate" is art recognized and includes a moiety that can be represented by the general formula:



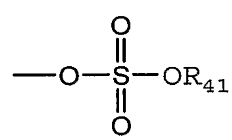
in which R_{41} is an electron pair, hydrogen, alkyl, cycloalkyl, or aryl.

What about PLA, PGA,PLGA, etc.

The terms triflyl, tosyl, mesyl, and nonaflyl are art-recognized and refer to trifluoromethanesulfonyl, *p*-toluenesulfonyl, methanesulfonyl, and nonafluorobutanesulfonyl groups, respectively. The terms triflate, tosylate, mesylate, and nonaflate are art-recognized and refer to trifluoromethanesulfonate ester, *p*-toluenesulfonate ester, methanesulfonate ester, and nonafluorobutanesulfonate ester functional groups and molecules that contain said groups, respectively.

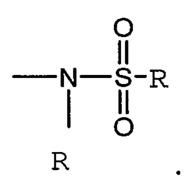
The abbreviations Me, Et, Ph, Tf, Nf, Ts, Ms represent methyl, ethyl, phenyl, trifluoromethanesulfonyl, nonafluorobutanesulfonyl, *p*-toluenesulfonyl and methanesulfonyl, respectively. A more comprehensive list of the abbreviations utilized by organic chemists of ordinary skill in the art appears in the first issue of each volume of the *Journal of Organic Chemistry*; this list is typically presentd in a table entitled Standard List of Abbreviations. The abbreviations contained in said list, and all abbreviations utilized by organic chemists of ordinary skill in the art are hereby incorporated by reference.

The term "sulfate" is art recognized and includes a moiety that can be represented by the general formula:

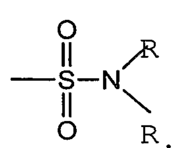


in which R_{41} is as defined above.

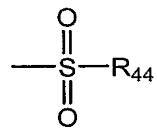
The term "sulfonylamino" is art recognized and includes a moiety that can be represented by the general formula:



The term "sulfamoyl" is art-recognized and includes a moiety that can be represented by the general formula:

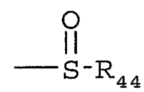


The term "sulfonyl", as used herein, refers to a moiety that can be represented by the general formula:



in which R_{44} is selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclyl, aryl, or heteroaryl.

The term "sulfoxido" as used herein, refers to a moiety that can be represented by the general formula:



in which R_{44} is selected from the group consisting of hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, heterocyclyl, aralkyl, or aryl.

A "selenoalkyl" refers to an alkyl group having a substituted seleno group attached thereto. Exemplary "selenoethers" which may be substituted on the alkyl are selected from one of -Se-alkyl, -Se-alkenyl, -Se-alkynyl, and -Se-$(CH_2)_m$-R_7, m and R_7 being defined above.

Analogous substitutions can be made to alkenyl and alkynyl groups to produce, for example, aminoalkenyls, aminoalkynyls, amidoalkenyls, amidoalkynyls, iminoalkenyls, iminoalkynyls, thioalkenyls, thioalkynyls, carbonyl-substituted alkenyls or alkynyls.

As used herein, the definition of each expression, e.g. alkyl, m, n, etc., when it occurs more than once in any structure, is intended to be independent of its definition elsewhere in the same structure.

It will be understood that "substitution" or "substituted with" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, e.g., which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc.

As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, those described herein above. The permissible substituents can be one or more

and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

The phrase "protecting group" as used herein means temporary substituents which protect a potentially reactive functional group from undesired chemical transformations. Examples of such protecting groups include esters of carboxylic acids, silyl ethers of alcohols, and acetals and ketals of aldehydes and ketones, respectively. The field of protecting group chemistry has been reviewed (Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991).

Certain compounds of the present invention may exist in particular geometric or stereoisomeric forms. The present invention contemplates all such compounds, including *cis*- and *trans*-isomers, *R*- and *S*-enantiomers, diastereomers, (D)-isomers, (L)-isomers, the racemic mixtures thereof, and other mixtures thereof, as falling within the scope of the invention. Additional asymmetric carbon atoms may be present in a substituent such as an alkyl group. All such isomers, as well as mixtures thereof, are intended to be included in this invention.

If, for instance, a particular enantiomer of a compound of the present invention is desired, it may be prepared by asymmetric synthesis, or by derivation with a chiral auxiliary, where the resulting diastereomeric mixture is separated and the auxiliary group cleaved to provide the pure desired enantiomers. Alternatively, where the molecule contains a basic functional group, such as amino, or an acidic functional group, such as carboxyl, diastereomeric salts are formed with an appropriate optically-active acid or base, followed by resolution of the diastereomers thus formed by fractional crystallization or chromatographic means well known in the art, and subsequent recovery of the pure enantiomers.

Contemplated equivalents of the compounds described above include compounds which otherwise correspond thereto, and which have the same general properties thereof (e.g., functioning as analgesics), wherein one or more simple variations of substituents are made which do not adversely affect the efficacy of the compound in binding to sigma receptors. In general, the compounds of the present invention may be prepared by the

methods illustrated in the general reaction schemes as, for example, described below, or by modifications thereof, using readily available starting materials, reagents and conventional synthesis procedures. In these reactions, it is also possible to make use of variants which are in themselves known, but are not mentioned here.

The term "alkali metal" refer to those elements listed in Group 1 of the periodic table. The following elements are alkali metals: Li, Na, K, Rb, Cs, and Fr.

For purposes of this invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 67th Ed., 1986-87, inside cover.

Exemplification

The invention now being generally described, it will be more readily understood by reference to the following examples, which are included merely for purposes of illustration of certain aspects and embodiments of the present invention, and are not intended to limit the invention.

Example 1

Synthesis of 2-[(*cis*-1,3-benzylidene glycerol)-2-propionic acid] - *cis*-1,3-*O*-Benzylidene glycerol (10.9 g, 60.4 mmol) was dissolved in 1,4-dioxane (250 mL) followed by the addition of NaH (7.0 g, 0.30 mol). The reaction mixture was stirred at rt for one hour before cooling to 0 °C. 2-Bromopropionic acid (8.64 mL, 96 mmol) was then added over a 15 minute period of time. The reaction mixture was allowed to return to rt and then stirred at 50 °C for 12 hours before it was cooled to 0 °C and quenched with ethanol followed by the addition of water (250 mL). The solution was adjusted to 4.0 pH using 1N HCl and extracted with CH_2Cl_2 (200 mL). This procedure was repeated once again after re-adjusting the pH to 4.0. The combined organic phase was dried with Na_2SO_4, gravity filtered, and evaporated. The solid was stirred in ethyl ether (50 mL) for 45 minutes and cooled to -25 °C for 3 hours before collecting 11.7 g of the white powder (77.3 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, 3, CH-C<u>H</u>$_3$, J=7.00 Hz), 3.46 (m, 1, -CH$_2$-C<u>H</u>-CH$_2$-, J=1.71 Hz), 4.04 (m, 2, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-, J=1.71 Hz), 4.22 (q, 1, C<u>H</u>-CH$_3$, J= 7.00 Hz), 4.29 (m, 2, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-, J=1.71 Hz), 5.54 (s, 1, C<u>H</u>), 7.34 (m, 3, arom. C<u>H</u>), 7.46 (m, 2, arom. C<u>H</u>). ^{13}C NMR (400 MHz, $CDCl_3$): δ 176.05 (<u>C</u>OOH), 137.82 (<u>C</u>H), 129.34 (<u>C</u>H), 128.52 (<u>C</u>H),

126.26 ($\underline{C}$H), 101.79 ($\underline{C}$H), 72.83 ($\underline{C}$H), 70.70 ($\underline{C}$H), 69.28 ($\underline{C}H_2$), 69.09 ($\underline{C}H_2$), 18.79 ($\underline{C}H_3$). FTIR: ν (cm^{-1}) 1714 (C=O), 1455 (CH_2 bend), 1401 (CH_3 bend). GC-MS 253 m/z (MH^+) (Theory: 252 m/z (M^+)). GC-MS 253 m/z (MH^+) (Theory: 252 m/z (M^+)) Elemental Analysis C: 61.75 %; H 6.37 % (Theory: C: 61.90 %; H 6.39 %).

Example 2

Synthesis of benzylidene protected [G0]-PGLLA-bzld - 2-[(*cis*-1,3-benzylidene glycerol)-2-propionic acid] (4.02 g, 15.9 mmol), *cis*-1,3-*O*-benzylideneglycerol (2.62 g, 14.5 mmol), and DPTS (1.21 g, 4.10 mmol) were dissolved in CH_2Cl_2 (40 mL). The reaction flask was flushed with nitrogen and then DCC (3.61 g, 17.5 mmol) was added. Stirring at room temperature was continued for 14 hours under a nitrogen atmosphere. Upon reaction completion, the DCC-urea was filtered and washed with a small amount of CH_2Cl_2 (10 mL) and the filtrate was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 MeOH:CH_2Cl_2. The product was dissolved in minimal CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at -20 °C to remove remaining DCC. Ethyl ether was decanted and the precipitate was exposed to reduced pressure to yield 5.63 g of a white powder (94.0 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56 (d, 6, CH-C$\underline{H}_3$, J=6.84 Hz), 3.47 (m, 2, -CH_2-C$\underline{H}$-CH_2-, J=1.71 Hz), 3.99 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-, J=1.71 Hz), 4.14 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-, J=1.71 Hz), 4.25 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.31 (m, 1, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.37 (q, 1, C$\underline{H}$-CH_3, J= 6.84 Hz), 4.42 (m, 1, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.72 (m, 1, -CH_2-C$\underline{H}$-CH_2-, J=1.71 Hz), 5.49 (s, 1, C$\underline{H}$), 5.53 (s, 1, C$\underline{H}$), 7.34 (m, 6, arom. C$\underline{H}$), 7.47 (m, 4, arom. C$\underline{H}$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.53 ($\underline{C}$OOR), 138.32 ($\underline{C}$H), 137.97 ($\underline{C}$H), 129.36 ($\underline{C}$H), 129.10 ($\underline{C}$H), 128.54 ($\underline{C}$H), 128.40 ($\underline{C}$H), 126.42 ($\underline{C}$H), 126.20 ($\underline{C}$H), 101.51 ($\underline{C}$H), 101.46 ($\underline{C}$H), 72.88 ($\underline{C}$H), 70.80 ($\underline{C}H_2$), 70.23 ($\underline{C}$H), 69.08 ($\underline{C}H_2$), 69.02 ($\underline{C}H_2$), 68.19 ($\underline{C}H_2$), 66.83 ($\underline{C}$H), 19.34 ($\underline{C}H_3$). FTIR: ν (cm^{-1}) 1743 (C=O), 1452 (CH_2 bend), 1389 (CH_3 bend). GC-MS 415 m/z (MH^+) (Theory: 414 m/z (M^+)) Elemental Analysis C: 66.63 %; H 6.33 % (Theory C: 66.65 %; H 6.32 %).

Example 3

Synthesis of [G0]-PGLLA-OH - Pd/C (10%) (10 % w/w) was added to a solution of benzylidene protected [G0]-PGLLA (5.49 g, 13.2 mmol) in EtOAc/MeOH (3:1, 40 mL). The flask was evacuated and filled with 50 psi of H_2 before shaking for 20 minutes. The catalyst was filtered and washed with EtOAc (10 mL). The filtrate was then evaporated to

give 2.94 g of a colorless, viscous oil (94.0 % yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.08 (m, 1, C<u>H</u>$_3$), 1.36 (m, 2, C<u>H</u>$_3$), 3.65 (broad m, 9, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.20 (broad m, 3, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-). ^{13}C NMR (400 MHz, $(CD_3)_2SO$): δ 174.03 (<u>C</u>OOR), 81.53 (<u>C</u>H), 76.66 (<u>C</u>H), 74.30 (<u>C</u>H), 61.82 (<u>C</u>H$_2$), 61.69 (<u>C</u>H$_2$), 60.37 (<u>C</u>H$_2$), 19.62 (<u>C</u>H$_3$). FTIR: ν (cm^{-}1) 3383 (OH), 1737 (C=O). GC MS 239 m/z (MH^+) (Theory: 238 m/z (M^+)) Elemental Analysis C: 45.52 %; H 7.65 % (Theory C: 45.37 %; H 7.62%).

Example 4

Synthesis of benzylidene protected [G1]-PGLLA-bzld - 2-[(*cis*-1,3-benzylidene glycerol)-2-propionic acid] (4.41 g, 17.50 mmol), [G0]-PGLLA (0.791 g, 3.32 mmol), and DPTS (2.46 g, 8.36 mmol), were dissolved in DMF (80 mL). The reaction flask was flushed with nitrogen and then DCC (5.31 g, 25.74 mmol) was added. The contents were stirred at room temperature for 14 hours under nitrogen atmosphere. The DMF was removed under high vacuum and the remaining residue was dissolved in CH_2Cl_2. The DCC-urea was filtered and washed with a small amount of CH_2Cl_2 (20 mL) and the filtrate was concentrated. The crude product was purified by silica gel chromatography, eluting with 3:97 MeOH:CH_2Cl_2. The product was dissolved in minimal CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at -20 °C to remove remaining DCC. Ethyl ether was decanted and the precipitate was exposed to reduced pressure to yield 3.45 g of a white powder (88.3 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 3, C<u>H</u>$_3$), 1.47 (m, 12, C<u>H</u>$_3$), 3.41 (m, 4, C<u>H</u>,), 3.76 (m, 2, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.97 (m, 4, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.10 (m, 4, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.28 (m, 20, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 5.30 (m, 1, C<u>H</u>), 5.49 (m, 4, C<u>H</u>), 7.30 (m, 12, arom. C<u>H</u>), 7.46 (m, 8, arom. C<u>H</u>). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.16 (<u>C</u>OOR), 138.24 (<u>C</u>H), 129.14 (<u>C</u>H), 128.40 (<u>C</u>H), 126.36 (<u>C</u>H), 101.47 (<u>C</u>H), 72.68 (<u>C</u>H), 70.54 (<u>C</u>H$_2$), 70.12 (<u>C</u>H), 68.13 (<u>C</u>H$_2$), 19.27 (<u>C</u>H$_3$), 18.99 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 1745 (C=O), 1451 (CH_2 bend), 1386 (CH_3 bend). FAB MS 1175.6 m/z (MH^+) (Theory: 1175.2 m/z (M^+)) Elemental Analysis C: 62.11 %; H 6.46 % (Theory C: 62.34 %; H 6.35%). SEC M_w: 1280, M_n: 1260, PDI: 1.01.

Example 5

Synthesis of [G1]-PGLLA-OH - Pd/C (10%) (10 % w/w) was added to a solution of benzylidene protected [G1]-PGLLA (0.270 g, 0.230 mmol) in THF (15 mL). The flask was evacuated and filled with 50 psi of H_2 before shaking for 15 minutes. The catalyst was

filtered and washed with THF (10 mL). The filtrate was then evaporated to give 0.178 g of a colorless, viscous oil (94.0 % yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.41 (m, 5, C<u>H</u>$_3$), 1.49 (m, 10, C<u>H</u>$_3$), 3.53 (m, 2, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.63 (m, 11, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.74 (m, 4, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.93 (m, 3, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.23 (m, 5, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.39 (m, 10, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-). ^{13}C NMR (400 MHz, CD_3Cl): δ 169.64 (<u>C</u>OOR), 74.53 (<u>C</u>H), 72.97 (<u>C</u>H), 72.74 (<u>C</u>H), 69.95 (<u>C</u>H$_2$), 68.97 (<u>C</u>H), 62.73 (<u>C</u>H$_2$), 61.76 (<u>C</u>H$_2$), 19.42 (<u>C</u>H$_3$), 18.13 (<u>C</u>H$_3$), 17.56 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 3409 (OH), 1733 (C=O), 1453 (CH_2 bend), 1374 (CH_3 bend). FAB MS 823.3 m/z (MH$^+$) (Theory: 822.8 m/z (M$^+$)) Elemental Analysis C: 47.72 %; H 7.41 % (Theory C: 48.17 %; H 7.11 %). SEC M_w: 1100, M_n: 1090, PDI: 1.01.

Example 6

Synthesis of benzylidene protected [G2]-PGLLA-bzld - 2-[(*cis*-1,3-benzylidene glycerol)-2-propionic acid] (8.029 g, 31.83 mmol), DCC (9.140 g, 44.30 mmol), and DPTS (4.629 g, 15.74 mmol) were dissolved in THF (80 mL). The reaction flask was flushed with nitrogen and stirred for 30 minutes before [G1]-PGLLA (0.825 g, 1.00 mmol) was added by dissolving in a minimal amount of THF. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. The DCC-urea was filtered and washed with a small amount of THF (20 mL). The THF filtrate was evaporated and the crude product was purified by silica gel chromatography, eluting with 3:97 MeOH:CH_2Cl_2. The product was dissolved in minimal CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at -20 °C to remove remaining DCC. Ethyl ether was decanted and the precipitate was exposed to reduced pressure to yield 2.09 g of a white powder (77 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 15, C<u>H</u>$_3$), 1.46 (m, 24, C<u>H</u>$_3$), 3.40 (m, 8, C<u>H</u>,), 3.77 (m, 5, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.95 (m, 10, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.06 (m, 12, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.28 (m, 47, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 5.49 (m, 8, C<u>H</u>), 7.30 (m, 24, arom. C<u>H</u>), 7.47 (m, 16, arom. C<u>H</u>). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.15 (<u>C</u>OOR), 138.28 (<u>C</u>H), 129.12 (<u>C</u>H), 128.40 (<u>C</u>H), 126.36 (<u>C</u>H), 101.44 (<u>C</u>H), 72.69 (<u>C</u>H), 70.54 (<u>C</u>H$_2$), 70.12 (<u>C</u>H), 68.13 (<u>C</u>H$_2$), 19.23 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 1746 (C=O), 1452 (CH_2 bend), 1386 (CH_3 bend). FAB MS 2697.0 m/z (MH$^+$) (Theory: 2696.8 m/z (M$^+$)) Elemental Analysis C: 60.86 %; H 6.37% (Theory C: 61.02 %; H 6.35 %). SEC M_w: 2350, M_n: 2310, PDI: 1.01.

Example 7

Synthesis of [G2]-PGLLA-OH - Pd/C (10%) (10 % w/w) was added to a solution of benzylidene protected [G2]-PGLLA (0.095 g, 0.035 mmol) in THF (10 mL). The flask was evacuated and filled with 50 psi of H_2 before shaking for 15 minutes. The catalyst was filtered and washed with THF (10 mL). The filtrate was evaporated to give 0.061 g of a colorless viscous oil (88.0 % yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.36 (m, 39, C<u>H</u>$_3$), 3.61 (m, 48, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.94 (m, 10, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.16 (m, 6, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.35 (m, 29, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-). ^{13}C NMR (400 MHz, $(CD_3)_2CO$): δ 174.37 (<u>C</u>OOR), 81.98 (<u>C</u>H), 74.16 (<u>C</u>H), 70.46 (<u>C</u>H), 62.32 (<u>C</u>H$_2$), 62.09 (<u>C</u>H$_2$), 18.76 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 3431 (OH), 1741 (C=O), 1453 (CH_2 bend), 1376 (CH_3 bend). MALDI-TOF MS 1991.8 m/z (MH^+) (Theory: 1991.9m/z (M^+)). SEC M_w: 2170, M_n: 2130, PDI: 1.01.

Example 8

Synthesis of [G2]-PGLLA-Ac - [G2]-PGLLA (0.098 g, 0.049 mmol) was dissolved in 5 mL of pyridine. Acetic anhydride (6.0 mL, 64 mmol) was then added via syringe and the reaction mixture was stirred at 40 °C for 8 hours. Pyridine and acetic anhydride were removed under high vacuum. The product was isolated on a prep TLC eluting with 4:96 MeOH: CH_3Cl. ^{1}H NMR (400 MHz, CD_3Cl): δ 1.22 (m, 15, C<u>H</u>$_3$), 1.39 (m, 24, C<u>H</u>$_3$), 2.05 (m, 48, C<u>H</u>$_3$), 3.62 - 4.21 (broad multiplets, 83, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-). ^{13}C NMR (400 MHz, CD_3Cl): δ 172.69 (<u>C</u>OOR), 170.87 (<u>C</u>OOR), 75.15 (<u>C</u>H), 74.60 (<u>C</u>H), 70.46 (<u>C</u>H), 63.68 (<u>C</u>H$_2$), 63.17 (<u>C</u>H$_2$), 29.88 (<u>C</u>H$_3$), 21.02 (<u>C</u>H$_3$), 19.01 (<u>C</u>H$_3$). FAB MS 2665.0 m/z (MH^+) (Theory: 2664.5 m/z (M^+)) Elemental Analysis C: 50.70 %; H 6.71 % (Theory C: 50.94 %; H 6.43 %).

Example 9

Synthesis of benzylidene protected [G3]-PGLLA-bzld - 2-[(*cis*-1,3-benzylidene glycerol)-2-propionic acid] (0.376 g, 1.49 mmol), DCC (0.463 g, 2.24 mmol), and DPTS (0.200 g, 0.680 mmol) were dissolved in THF (15 mL). The reaction flask was flushed with nitrogen and stirred for 1.5 hours before [G2]-PGLLA (0.070 g, 0.035 mmol) was added by dissolving in a minimal amount of THF. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. The DCC-urea was filtered and washed with a small amount of THF (20 mL). The THF filtrate was evaporated and the crude product was purified by silica gel chromatography, eluting with 3:97 MeOH:CH_2Cl_2. The product was dissolved in minimal CH_2Cl_2, filtered (to remove any DCU), and

precipitated in ethyl ether at -20 °C to remove remaining DCC. Ethyl ether was decanted and the precipitate was exposed to reduced pressure to yield 0.164 g of a white powder (89.1 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (m, 39, C<u>H</u>$_3$), 1.45 (m, 48, C<u>H</u>$_3$), 3.38 (m, 16, C<u>H</u>,), 3.77 (m, 14, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 3.97 (m, 20, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.07 (m, 24, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.24 (m, 97, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 4.39 (m, 8, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$-), 5.47 (m, 16, C<u>H</u>), 7.31 (m, 48, arom. C<u>H</u>), 7.44 (m, 32, arom. C<u>H</u>). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.14 (<u>C</u>OOR), 138.28 (<u>C</u>H), 129.12 (<u>C</u>H), 128.40 (<u>C</u>H), 126.36 (<u>C</u>H), 101.41 (<u>C</u>H), 72.68 (<u>C</u>H), 70.56 (<u>C</u>H$_2$), 70.13 (<u>C</u>H), 68.11 (<u>C</u>H$_2$), 19.25 (<u>C</u>H$_3$), 19.02 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 1744 (C=O), 1451 (CH_2 bend), 1385 (CH_3 bend). MALDI MS 5743.3 m/z (MH^+) (Theory: 5739.9 m/z (M^+)) Elemental Analysis C: 60.32 %; H 6.34% (Theory C: 60.47 %; H 6.36 %). SEC M_w: 4370, M_n: 4310, PDI: 1.01.

Example 10

Synthesis of [G3]-PGLLA-OH - Pd/C (10%) (10 % w/w) was added to a solution of benzylidene protected [G3]-PGLLA (0.095 g, 0.035 mmol) in THF (15 mL). The flask was evacuated and filled with 50 psi of H_2 before shaking for 15 minutes. The catalyst was filtered and washed with THF (10 mL). The filtrate was evaporated to give 0.128 g of a colorless viscous oil (95.4 % yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 1.37 (m, 87, C<u>H</u>$_3$), 3.56 (m, 83, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$- or -C<u>H</u>-CH$_3$), 3.78 (m, 13, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$- or -C<u>H</u>-CH$_3$), 4.01 (m, 14, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$- or -C<u>H</u>-CH$_3$), 4.18 (m, 13, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$- or -C<u>H</u>-CH$_3$), 4.39 (m, 56, -C<u>H</u>$_2$-C<u>H</u>-C<u>H</u>$_2$- or -C<u>H</u>-CH$_3$). ^{13}C NMR (400 MHz, $(CD_3)_2CO$): δ 174.37 (<u>C</u>OOR), 82.01 (<u>C</u>H), 74.16 (<u>C</u>H), 62.35 (<u>C</u>H$_2$), 62.15 (<u>C</u>H$_2$), 18.80 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 3434 (OH), 1738 (C=O), 1452 (CH_2 bend), 1376 (CH_3 bend). MALDI MS 4332.5 m/z (MH^+) (Theory: 4330.2 m/z (M^+)) Elemental Analysis C: 49.56 %; H 7.21 % (Theory C: 49.09 %; H 6.94%). SEC M_w: 4110, M_n: 4060, PDI: 1.01.

Example 11

Synthesis of [G0]-PGLSA-bzld - Succinic acid (1.57 g, 13.3 mmol), *cis*-1,3-*O*-benzylideneglycerol (5.05 g, 28.0 mmol), and DPTS (4.07 g, 13.8 mmol) were dissolved in CH_2Cl_2 (120 mL). The reaction flask was flushed with nitrogen and then DCC (8.19 g, 39.7 mmol) was added. Stirring at room temperature was continued for 14 hours under a nitrogen atmosphere. Upon reaction completion, the DCC-urea was filtered and washed with a small amount of CH_2Cl_2 (20 mL). The crude product was purified by silica gel

chromatography, eluting with 3:97 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. Following vacuum filtration, 5.28 g of a white solid was collected (90 % yield). ^{1}H NMR ($CDCl_3$): δ 2.78 (s, 4, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.08 (m, 4, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.23 (m, 4, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.69 (m, 2, -CH_2-C$\underline{H}$-CH_2-, J=1.54 Hz, 1.71 Hz), 5.50 (s, 2, C$\underline{H}$), 7.34 (m, 6, arom. C$\underline{H}$), 7.48 (m, 4, arom. C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 172.32 ($\underline{C}$OOR), 138.03 ($\underline{C}$H), 129.23 ($\underline{C}$H), 128.48 ($\underline{C}$H), 126.24 ($\underline{C}$H), 101.33 ($\underline{C}$H), 69.16 ($\underline{C}H_2$), 66.50 ($\underline{C}$H), 29.57 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 2992 (aliph. C-H stretch), 1727 (C=O). GC-MS 443 m/z (MH^+) (Theory: 442 m/z (M^+)). HR FAB 442.1635 m/z (M^+) (Theory: 442.1628 m/z (M^+)). Elemental Analysis C: 65.25 %; H 5.85 % (Theory C: 65.15 %; H 5.92 %).

Example 12

Synthesis of [G0]-PGLSA-OH - Pd/C (10 % w/w) was added to a solution of benzylidene protected [G0]-PGLSA (2.04 g, 4.61 mmol) in THF (30 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF (20 mL). The filtrate was evaporated to give 1.18 g of a clear viscous oil (97 % yield). ^{1}H NMR (CD_3OD): δ 2.67 (s, 4, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.64 (m, 8, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.87 (m, 2, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR (CD_3OD): □ 172.77 ($\underline{C}$OOR), 75.84 ($\underline{C}H_2$), 60.41 ($\underline{C}$H), 28.96 ($\underline{C}H_2$). ^{13}C NMR ($(CD_3)_2CO$): δ 171.99 ($\underline{C}$OOR), 76.15 ($\underline{C}H_2$), 60.89 ($\underline{C}$H). FTIR: ν (cm^{-1}) 3299 (OH), 1728 (C=O). GC-MS 284 m/z ($M+NH_4^+$) (Theory: 266 m/z (M^+)). Elemental Analysis C: 44.94 %; H 6.87 % (Theory C: 45.11 %; H 6.81%).

Example 13

Synthesis of 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester - *cis*-1,3-*O*-Benzylideneglycerol (9.90 g, 54.9 mmol) was dissolved in pyridine (100 mL) followed by the addition of succinic anhydride (8.35 g, 83.4 mmol). The reaction mixture was stirred at room temperature for 18 hours before the pyridine was removed under vacuum at 40 °C. The remaining solid was dissolved in CH_2Cl_2 (100 mL) and washed three times with cold 0.2 N HCl (100 mL), or until the aqueous phase remained at pH 1. The organic phase was evaporated and the solid was dissolved in deionized water (300 mL). 1 N NaOH was added until pH 7 was obtained and the product was dissolved in solution. The aqueous phase was extracted with CH_2Cl_2 (200 mL) and then readjusted to pH 4. The aqueous phase was

subsequently extracted twice with CH_2Cl_2 (200 mL), dried with Na_2SO_4, filtered, and evaporated. The solid was stirred in ethyl ether (50 mL) and cooled to -25 °C for 3 hours before collecting 14.6 g of a white powder (95 % yield). ^{1}H NMR ($CDCl_3$): δ 2.68 (m, 4, $-C\underline{H}_2-C\underline{H}_2-$), 4.13 (m, 2, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.33 (m, 2, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.70 (m, 1, $-CH_2-C\underline{H}-CH_2-$), 5.51 (s, 1, $C\underline{H}$), 7.34 (m, 3, arom. $C\underline{H}$), 7.47 (m, 2, arom. $C\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 178.07 ($\underline{C}OOH$), 172.38 ($\underline{C}OOR$), 137.95 ($\underline{C}H$), 129.33 ($\underline{C}H$), 128.51 ($\underline{C}H$), 126.26 ($\underline{C}H$), 101.43 ($\underline{C}H$), 69.15 ($\underline{C}H_2$), 66.57 ($\underline{C}H$), 29.24 ($\underline{C}H_2$), 29.05 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 2931 (aliph. C-H stretch), 1713 (C=O). GC-MS 281 m/z (MH^+) (Theory: 280 m/z (M^+)). Elemental Analysis C: 60.07 %; H 5.80 % (Theory: C: 59.99 %; H 5.75 %).

Example 14

Synthesis of [G1]-PGLSA-bzld - 2-(*cis*-1,3-*O*-Benzylidene glycerol)succinic acid mono ester (6.33 g, 22.6 mmol), [G0]-PGLSA (1.07 g, 4.02 mmol), and DPTS (2.51 g, 8.53 mmol) were dissolved in THF (60 mL). The reaction flask was flushed with nitrogen and then DCC (7.04 g, 34.1 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 to 5:95 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. The ethyl ether was decanted and the precipitate was isolated to yield 5.11 g of a white powder (97 % yield). ^{1}H NMR ($CDCl_3$): δ 2.58 (m, 4, $-C\underline{H}_2-C\underline{H}_2-$), 2.63 (m, 8, $-C\underline{H}_2-C\underline{H}_2-$), 2.71 (m, 8, $-C\underline{H}_2-C\underline{H}_2-$), 4.12 (m, 12, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.23 (m, 12, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.69 (m, 4, $-CH_2-C\underline{H}-CH_2-$), 5.20 (m, 2, $-CH_2-C\underline{H}-CH_2-$), 5.51 (m, 4, $C\underline{H}$), 7.33 (m, 12, arom. $C\underline{H}$), 7.46 (m, 8, arom. $C\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 172.28 ($\underline{C}OOR$), 171.91 ($\underline{C}OOR$), 171.53 ($\underline{C}OOR$), 138.03 ($\underline{C}H$), 129.26 ($\underline{C}H$), 128.48 ($\underline{C}H$), 126.22 ($\underline{C}H$), 101.32 ($\underline{C}H$), 69.50 ($\underline{C}H$), 69.16 ($\underline{C}H_2$), 66.54 ($\underline{C}H$), 62.49 ($\underline{C}H_2$), 29.36 ($\underline{C}H_2$), 29.03 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 2858 (aliph. C-H stretch), 1731 (C=O). FAB MS 1315.6 m/z (MH^+) (Theory: 1315.3 m/z (M^+)). Elemental Analysis C: 60.13 %; H 5.82 % (Theory C: 60.27 %; H 5.67%). SEC M_w: 1460, M_n: 1450, PDI: 1.01.

Example 15

Synthesis of [G1]-PGLSA-OH - Pd/C (10 % w/w) was added to a solution of benzylidene protected [G1]-PGLSA (0.270 g, 0.230 mmol) in THF (20 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF (20 mL). The filtrate was evaporated to give 0.178 g of a colorless, viscous oil (94 % yield). ^{1}H NMR (CD_3OD): δ 2.63 (m, 20, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.52 (m, 4, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 3.64 (m, 8, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 3.80 (m, 2, -CH$_2$-C<u>H</u>-CH$_2$-), 4.05 (m, 2, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.14 (m, 2, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.21 (m, 4, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.30 (m, 4, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.85 (m, 2, -CH$_2$-C<u>H</u>-CH$_2$-), 5.25 (m, 2, -CH$_2$-C<u>H</u>-CH$_2$-). ^{13}C NMR (CD_3OD): δ 172.82 (<u>C</u>OOR), 172.58 (<u>C</u>OOR), 172.48 (<u>C</u>OOR), 172.08 (<u>C</u>OOR), 75.82 (<u>C</u>H), 69.90 (<u>C</u>H), 69.68 (<u>C</u>H), 65.66 (<u>C</u>H$_2$), 62.85 (<u>C</u>H$_2$), 62.30 (<u>C</u>H$_2$), 60.43 (<u>C</u>H$_2$), 28.83 (<u>C</u>H$_2$), 28.61 (<u>C</u>H$_2$). FTIR: ν (cm^{-1}) 3405 (OH), 2943 (aliph. C-H stretch), 1726 (C=O). FAB MS 963.2 m/z (MH$^+$) (Theory: 962.9 m/z (M$^+$)). Elemental Analysis C: 47.13 %; H 6.11 % (Theory C: 47.40 %; H 6.07 %). SEC M_w: 1510, M_n: 1500, PDI: 1.01.

Example 16

Synthesis of [G2]-PGLSA-bzld - 2-(*cis*-1,3-*O*-Benzylidene glycerol)succinic acid mono ester (4.72 g, 16.84 mmol), [G1]-PGLSA (1.34 g, 1.39 mmol), and DPTS (1.77 g, 6.02 mmol) were dissolved in THF (100 mL). The reaction flask was flushed with nitrogen and then DCC (4.62 g, 22.4 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 to 5:95 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. The ethyl ether was decanted and the precipitate was isolated to yield 4.00 g of a white powder (94 % yield). ^{1}H NMR ($CDCl_3$): δ 2.59 (broad m, 26, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 2.69 (broad m, 52, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 4.13 (m, 28, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.13 (m, 28, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.69 (m, 8, -CH$_2$-C<u>H</u>-CH$_2$-), 5.22 (m, 6, -CH$_2$-C<u>H</u>-CH$_2$-), 5.50 (s, 8, C<u>H</u>), 7.32 (m, 24, arom. C<u>H</u>), 7.47 (m, 16, arom. C<u>H</u>). ^{13}C NMR ($CDCl_3$): δ 172.27 (<u>C</u>OOR), 171.88 (<u>C</u>OOR), 171.60 (<u>C</u>OOR), 138.04 (<u>C</u>H), 129.25 (<u>C</u>H), 128.47 (<u>C</u>H), 126.21 (<u>C</u>H), 101.30 (<u>C</u>H), 69.48 (<u>C</u>H), 69.15 (<u>C</u>H$_2$), 66.54 (<u>C</u>H), 62.57 (<u>C</u>H$_2$), 29.35 (<u>C</u>H$_2$), 29.18 (<u>C</u>H$_2$) 29.03 (<u>C</u>H$_2$), 28.84 (<u>C</u>H$_2$). FTIR: γcm^{-1}) 2969 (aliph. C-H stretch), 1733 (C=O). FAB MS 3060.7 m/z (MH$^+$) (Theory: 3060.9 m/z

(M^+)). Elemental Analysis C: 59.20 %; H 5.64 % (Theory C: 58.86 %; H 5.60 %). SEC M_w: 3030, M_n: 2990, PDI: 1.01.

Example 17

Synthesis of [G2]-PGLSA-OH - Pd/C (10 % w/w) was added to a solution of benzylidene protected [G2]-PGLSA (2.04 g, 0.667 mmol) in THF (20 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF (20 mL). The filtrate was evaporated to give 1.49 g of a colorless, viscous oil (95 % yield). ^{1}H NMR (CD_3OD): δ 2.64 (m, 52, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.53 (m, 16, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 3.64 (m, 4, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 3.80 (m, 8, -CH$_2$-C<u>H</u>-CH$_2$-), 4.06 (m, 8, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.14 (m, 6, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.21 (m, 11, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.30 (m, 11, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 5.25 (m, 6, -CH$_2$-C<u>H</u>-CH$_2$-). ^{13}C NMR (CD_3OD): δ 172.83 (<u>C</u>OOR), 172.59 (<u>C</u>OOR), 172.49 (<u>C</u>OOR), 69.91 (<u>C</u>H), 69.69 (<u>C</u>H), 65.68 (<u>C</u>H$_2$), 62.88 (<u>C</u>H$_2$), 62.37 (<u>C</u>H$_2$), 28.61 (<u>C</u>H$_2$). FTIR: ν (cm^{-1}) 3429 (OH), 2952 (aliph. C-H stretch), 1728 (C=O). MALDI MS 2357.3 m/z (MH^+) (Theory: 2356.1 m/z (M^+)). Elemental Analysis C: 48.32 %; H 5.97 % (Theory C: 47.92 %; H 5.90%). SEC M_w: 3060, M_n: 3000, PDI: 1.02.

Example 18

Synthesis of succinic acid monomethallyl ester (SAME) - 2-Methyl-2-propen-1-ol (4.90 mL, 58.2 mmol) was dissolved in pyridine (20 mL) followed by the addition of succinic anhydride (7.15 g, 71.4 mmol). The reaction mixture was stirred at room temperature for 15 hours before the pyridine was removed under vacuum at 30 °C. The remaining liquid was dissolved in CH_2Cl_2 (100 mL) and washed two times with cold 0.2 N HCl (100 mL). The organic phase was dried with Na_2SO_4, gravity filtered, and evaporated to give 9.25 g of a clear liquid (92 % yield). ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 3, C<u>H</u>$_3$), 2.64 (m, 4, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 4.48 (s, 2, -CH$_2$-), 4.88 (m, 1, vinyl C<u>H</u>$_2$), 4.93 (m, 1, vinyl C<u>H</u>$_2$). ^{13}C NMR ($CDCl_3$): δ 178.58 (<u>C</u>OOH), 172.05 (<u>C</u>OOR), 139.88 (<u>C</u>H), 113.31 (<u>C</u>H$_2$), 68.31 (<u>C</u>H$_2$), 29.11 (<u>C</u>H$_2$), 28.99 (<u>C</u>H$_2$), 19.59 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 2939 (aliph. C-H stretch), 1711 (C=O). GC-MS 173 m/z (MH^+) (Theory: 172 m/z (M^+)). Elemental Analysis C: 55.51 %; H 7.09 % (Theory: C: 55.81 %; H 7.02 %).

Example 19

Synthesis of [G2]-PGLSA-SAME - Succinic acid monomethallyl ester (0.826 g, 4.80 mmol), [G2]-PGLSA (0.401 g, 0.170 mmol), and DPTS (0.712 g, 2.42 mmol) were dissolved in THF (50 mL). The reaction flask was flushed with nitrogen and then DCC (1.52 g, 7.37 mmol) was added. Stirring at room temperature was continued for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of CH_2Cl_2 (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 to 5:95 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. The ethyl ether was decanted and the precipitate was isolated to yield 0.558 g of a clear colorless oil (68.2 % yield). ^{1}H NMR ($CDCl_3$): δ1.72 (s, 48, C$\underline{H}_3$), 2.63 (m, 116, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.16 (m, 23, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.27 (m, 23, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.48 (s, 32, -C$\underline{H}_2$-), 4.89 (s, 16, vinyl C$\underline{H}_2$), 4.94 (s, 16, vinyl C$\underline{H}_2$), 5.24 (m, 14, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR ($CDCl_3$): δ 171.91 ($\underline{C}$OOR), 171.67 ($\underline{C}$OOR), 139.98 ($\underline{C}$H), 113.22 ($\underline{C}H_2$), 69.43 ($\underline{C}$H), 68.31 ($\underline{C}H_2$), 62.56 ($\underline{C}H_2$), 29.10 ($\underline{C}H_2$), 29.02 ($\underline{C}H_2$) 28.83 ($\underline{C}H_2$), 19.66 ($\underline{C}H_3$). FTIR: ν (χm^{-1}) 2969 (aliph. C-H stretch), 1734 (C=O). MALDI MS 4840.9 m/z (MH^+) (Theory: 4838.7 m/z (M^+)). Elemental Analysis C: 55.37 %; H 6.22 % (Theory C: 55.35%; H 6.29%). SEC M_w: 5310, M_n: 5230, PDI: 1.02.

Example 20

Synthesis of [G3]-PGLSA-bzld - 2-(*cis*-1,3-*O*-Benzylidene glycerol)succinic acid mono ester (2.77 g, 9.89 mmol), [G2]-PGLSA (1.00 g, 0.425 mmol), and DPTS (1.30 g, 4.42 mmol) were dissolved in THF (40 mL). The reaction flask was flushed with nitrogen and then DCC (2.67 g, 12.9 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 to 5:95 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. The ethyl ether was decanted and the precipitate was isolated to yield 3.51 g of a white powder (90 % yield). ^{1}H NMR ($CDCl_3$): δ 2.57 – 2.72 (broad m, 116, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.12 (m, 60, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.23 (m, 60, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.68 (m, 16, -CH_2-C$\underline{H}$-CH_2-), 5.22 (m, 14, -CH_2-C$\underline{H}$-CH_2-), 5.49 (s, 16, C$\underline{H}$), 7.33 (m, 48, arom. C$\underline{H}$), 7.46 (m, 32, arom. C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 172.31 ($\underline{C}$OOR), 171.97 ($\underline{C}$OOR), 171.65 ($\underline{C}$OOR), 138.01 ($\underline{C}$H), 129.28 ($\underline{C}$H), 128.49

($\underline{C}H$), 126.21 ($\underline{C}H$), 101.28 ($\underline{C}H$), 69.45 ($\underline{C}H$), 69.16 ($\underline{C}H_2$), 66.53 ($\underline{C}H$), 62.59 ($\underline{C}H_2$), 29.32 ($\underline{C}H_2$), 29.16 ($\underline{C}H_2$) 29.01 ($\underline{C}H_2$), 28.81 ($\underline{C}H_2$). FTIR: γcm^{-1}) 2984 (aliph. C-H stretch), 1733 (C=O). MALDI MS 6553.4 m/z (MH^+) (Theory: 6552.2 m/z (M^+)). Elemental Analysis C: 58.50 %; H 5.66 % (Theory C: 58.29 %; H 5.57 %). SEC M_w: 5550, M_n: 5480, PDI: 1.01.

Example 21

Synthesis of [G3]-PGLSA-OH - Pd/C (10 % w/w) was added to a solution of benzylidene protected [G3]-PGLSA (1.23 g, 0.188 mmol) in 9:1 THF/MeOH (20 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with 9:1 THF/MeOH (20 mL). The filtrate was evaporated to give 0.923 g of a colorless, viscous oil (95 % yield). ^1H NMR (CD_3OD): δ 2.64 (m, 116, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.51 (m, 26, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 3.67 (m, 28, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 3.80 (m, 12, -CH$_2$-C$\underline{H}$-CH$_2$-), 4.05 (m, 14, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.14 (m, 14, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.22 (m, 22, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.30 (m, 22, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 5.26 (m, 14, -CH$_2$-C$\underline{H}$-CH$_2$). ^{13}C NMR (CD_3OD): δ 172.86 ($\underline{C}OOR$), 69.91 ($\underline{C}H$), 67.64 ($\underline{C}H$), 65.67 ($\underline{C}H_2$), 62.87 ($\underline{C}H_2$), 62.41 ($\underline{C}H_2$), 28.61 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 3442 (OH), 2959 (aliph. C-H stretch), 1731 (C=O). MALDI MS 5144.8 m/z (MH^+) (Theory: 5142.5 m/z (M^+)). Elemental Analysis C: 48.07 %; H 5.84 % (Theory C: 48.11 %; H 5.84 %). SEC M_w: 5440, M_n: 5370, PDI: 1.01.

Example 22

Synthesis of [G4]-PGLSA-bzld - 2-(*cis*-1,3-*O*-Benzylidene glycerol)succinic acid mono ester (2.43 g, 8.67 mmol), [G3]-PGLSA (0.787 g, 0.153 mmol), and DPTS (1.30 g, 4.42 mmol) were dissolved in 10:1 THF/DMF (40 mL). The reaction flask was flushed with nitrogen and then DCC (2.63 g, 12.7 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, solvents were removed under vacuum and the remaining solids were redissolved CH_2Cl_2. The DCC-urea was filtered and washed with a small amount of CH_2Cl_2 (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 to 5:95 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. The ethyl ether was decanted and the precipitate was exposed to reduced pressure to yield 1.50 g of a white powder (73 % yield). ^1H NMR ($CDCl_3$): δ 2.63 (m, 70, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.72 (m, 146, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.90 (m, 32, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.14 (m, 100, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.25 (m, 100, -C$\underline{H}_2$-

CH-C$\underline{H}_2$-), 4.70 (m, 32, -CH_2-C$\underline{H}$-CH_2-), 5.25 (m, 16, -CH_2-C$\underline{H}$-CH_2-), 5.52 (s, 32, C$\underline{H}$), 7.33 (m, 96, arom. C$\underline{H}$), 7.47 (m, 64, arom. C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 172.27 ($\underline{C}$OOR), 171.90 ($\underline{C}$OOR), 171.57 ($\underline{C}$OOR), 138.08 ($\underline{C}$H), 129.25 ($\underline{C}$H), 128.47 ($\underline{C}$H), 126.23 ($\underline{C}$H), 101.27 ($\underline{C}$H), 69.49 ($\underline{C}$H), 69.13 ($\underline{C}H_2$), 66.54 ($\underline{C}$H), 62.45 ($\underline{C}H_2$), 29.34 ($\underline{C}H_2$), 29.02 ($\underline{C}H_2$), 28.83 ($\underline{C}H_2$). FTIR: ν (χm^{-1}) 2978 (aliph. C-H stretch), 1733 (C=O). MALDI MS 13536.8 m/z (MH^+) (Theory: 13534.7 m/z (M^+)). Elemental Analysis C: 58.20 %; H 5.56 % (Theory C: 58.04 %; H 5.56 %). SEC M_w: 9000, M_n: 8900, PDI: 1.01.

Example 23

Synthesis of [G4]-PGLSA-OH - Pd/C (10 % w/w) was added to a solution of benzylidene protected [G4]-PGLSA (0.477 g, 0.0352 mmol) in 9:1 THF/MeOH (20 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with 9:1 THF/MeOH (20 mL). The filtrate was evaporated to give 0.351 g of a colorless, viscous oil (93 % yield). ^{1}H NMR (CD_3OD): δ 2.65 (m, 244, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.53 (m, 50, -C$\underline{H}_2$-CH-C$\underline{H}_2$), 3.65 (m, 22, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 3.81 (m, 28, -CH_2-C$\underline{H}$-CH_2-), 4.05 (m, 32, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.14 (m, 32, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.24 (m, 60, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.30 (m, 60, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 5.26 (m, 32, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR (CD_3OD): δ 172.94 ($\underline{C}$OOR), 69.92 ($\underline{C}$H), 65.72 ($\underline{C}H_2$), 62.91 ($\underline{C}H_2$), 28.67 ($\underline{C}H_2$). FTIR: □ (cm^{-1}) 3444 (OH), 2931 (aliph. C-H stretch), 1729 (C=O). MALDI MS 10715.6 m/z (MH^+) (Theory: 10715.3 m/z (M^+)). Elemental Analysis C: 48.50 %; H 5.83 % (Theory C: 48.20 %; H 5.81 %). SEC M_w: 8800, M_n: 8720, PDI: 1.01.

Example 24

The PGLSA dendrimers or other dendrimers described herein can also be synthesized through Accelerated Syntheses for example:

Example 24.1 Synthesis of 2-(cis-1,3-O-benzylidene glycerol)succinic acid mono ester anhydride - 2-(*cis*-1,3-*O*-Benzylidene glycerol)succinic acid mono ester (50.00 g, 178.4 mmol)) and DCC (22.09 g, 107.0 mmol) were dissolved in DCM (300 mL) and stirred for 14 hours. The DCU precipitate was collected by filtration and washed with DCM (50 mL). The organic phase was directly added to 900 mL of hexanes. The hexanes and precipitate were cooled to –20 °C for 3 hours before 46.11 g of precipitate was collected after filtration (95 % yield). ^{1}H NMR ($CDCl_3$): δ 2.75 (m, 4, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.12 (m, 4, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.25 (m, 4, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.71 (m, 2, -CH_2-C$\underline{H}$-CH_2-), 5.52 (s, 2, C$\underline{H}$), 7.34 (m, 6, arom.

C<u>H</u>), 7.47 (m, 4, arom. C<u>H</u>). ^{13}C NMR ($CDCl_3$): δ 171.77 (<u>C</u>OOR), 167.99 (-<u>C</u>OOCO-), 137.96 (<u>C</u>H), 129.29 (<u>C</u>H), 128.51 (<u>C</u>H), 126.20 (<u>C</u>H), 101.36 (<u>C</u>H), 69.13 (<u>C</u>H_2), 66.76 (<u>C</u>H), 30.37 (<u>C</u>H_2), 28.94 (<u>C</u>H_2). FTIR: ν (cm^{-1}) 2938 (aliph. C-H stretch), 1815 (C=O), 1730 (C=O). FAB-MS 543.2 m/z $[M-H]^+$ (Theory: 542.53 m/z $[M]^+$). Elemental Analysis C: 61.83 %; H 5.70 % (Theory: C: 61.99 %; H 5.57 %).

Example 24.2 Synthesis of [G1]-PGLSA-bzld - $Pd(OH)_2/C$ (10% w/w) and activated carbon were added to a solution of [G0]-PGLSA-bzld (3.571 g, 8.071 mmol) in THF (25 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst and activated carbon were filtered off and washed with THF (50 mL). 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (21.990 g, 40.532 mmol) and then DMAP (0.514 g, 4.207 mmol) were directly added to the deprotected core in the THF (more THF was added to give a total volume of 100 mL). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Any remaining anhydride was quenched by the addition of n-propanol (4.0 mL, 44 mmol), which was allowed to stir for another 5 hours. The THF was removed under vacuum and the remaining contents were dissolved in DCM (250 mL) and washed once with 0.1 N HCl (200 mL) and three times with saturated sodium bicarbonate (200 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the dendrimer was precipitated in hexanes (450 mL) and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 10.29 g of a white solid (96.9 % yield). ^1H NMR, ^{13}C NMR, FTIR, MALDI-TOF MS, Elemental Analysis, and SEC have been previously reported. T_g (°C): 36.7 to 42.4, 39.5 at half-height.

Example 24.3 Synthesis of [G2]-PGLSA-bzld (186) - $Pd(OH)_2/C$ (10% w/w) and activated carbon were added to a solution of [G1]-PGLSA-bzld (4.40 g, 3.43 mmol) in THF (50 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst and activated carbon were filtered off and washed with THF (50 mL). 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (18.459 g, 34.024 mmol) and then DMAP (0.831 g, 6.802 mmol) were directly added to the deprotected dendrimer in the THF. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Any remaining anhydride was quenched by the addition of n-propanol (3.0 mL, 33 mmol), which was allowed to stir for another 5 hours. The THF was removed under vacuum and the remaining contents were dissolved in DCM (400 mL) and washed once with 0.1 N HCl (300 mL) and three times with saturated sodium

bicarbonate (300 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the dendrimer was precipitated in hexanes (900 mL) and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 9.85 g of a white solid (96.2 % yield). ^1H NMR, ^{13}C NMR, FTIR, MALDI-TOF MS, Elemental Analysis, and SEC have been previously reported. T_g (°C): 39.3 to 45.4, 42.3 at half-height.

Example 24.4 Synthesis of [G3]-PGLSA-bzld - $Pd(OH)_2/C$ (10% w/w) and activated carbon were added to a solution of [G2]-PGLSA-bzld (12.81 g, 4.218 mmol) in THF (100 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst and activated carbon were filtered off and washed with THF (100 mL). From this solution, 1.822 g of [G2]-PGLSA-OH in THF was removed form the mixture. Next, 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (45.9154 g, 84.632 mmol) and then DMAP (1.5592 g, 12.763 mmol) were directly added to the deprotected core in the THF. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Any remaining anhydride was quenched by the addition of n-propanol (8.0 mL, 88 mmol), which was allowed to stir for another 5 hours. The THF was removed under vacuum and the remaining contents were dissolved in DCM (500 mL) and washed once with 0.1 N HCl (400 mL) and three times with saturated sodium bicarbonate (400 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the dendrimer was precipitated in hexanes (800 mL) and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 20.37 g of a white solid (91.4 % yield). ^1H NMR, ^{13}C NMR, FTIR, MALDI-TOF MS, Elemental Analysis, and SEC have been previously reported. T_g (°C): 43.1 to 48.3, 45.7 at half-height.

Example 24.5 Synthesis of [G3]-PGLSA-OH - $Pd(OH)_2/C$ (10% w/w) and activated carbon were added to a solution of [G3]-PGLSA-bzld (3.571 g, 8.071 mmol) in THF/MeOH (9:1) (25 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst and activated carbon were filtered off and washed with more of the THF/MeOH solution (50 mL) before the solvents were evaporated. The product was used directly in next reaction

Example 24.6 Synthesis of [G4]-PGLSA-bzld – The deprotected core was dissolved in the THF/dimethyl acetimide (10:1) (200 mL) and 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (60.83 g, 0.11212 mmol) and then DMAP (1.63 g, 13.342 mmol) were directly added to the reaction flask. The reaction was stirred at

room temperature for 14 hours under nitrogen atmosphere. Any remaining anhydride was quenched by the addition of n-propanol (4.0 mL, 44 mmol), which was allowed to stir for another 5 hours. The solvents were removed under vacuum and the remaining contents were dissolved in DCM (250 mL) and washed once with 0.1 N HCl (200 mL) and three times with saturated sodium bicarbonate (200 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the dendrimer was precipitated in hexanes (450 mL) and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 33.25 g of a white solid (88.15 % yield). ^{1}H NMR, ^{13}C NMR, FTIR, MALDI-TOF MS, Elemental Analysis, and SEC have been previously reported. T_g (°C): 43.6 to 49.6, 47.0 at half-height.

Example 24.7 Synthesis of [G5]-PGLSA-bzld - [G4]-PGLSA-OH (0.2052 g, 0.0192 mmol) and 2-(*cis*-1,3-*O*-Benzylidene glycerol)succinic acid mono ester anhydride (0.067 g, 0.548 mmol), were dissolved in 1:1 THF/DMF (15 mL). DMAP (1.152 g, 2.123 mmol) was added and the reaction flask was flushed with nitrogen. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Any remaining anhydride was quenched by the addition of water (4.0 mL) which was allowed to stir for another 5 hours. The solvents were removed under vacuum and the remaining contents were dissolved in DCM (150 mL) and washed once with 0.1 N HCl (100 mL) and three times with saturated sodium bicarbonate (100 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the dendrimer was precipitated in hexanes (450 mL) and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 0.414 g of a white solid (78.6 % yield). ^{1}H NMR ($CDCl_3$): δ 2.57-2.69 (broad m, 488, -CH_2-CH_2-), 4.07-4.21 (m, 507, -CH_2-CH-CH_2-), 4.66 (m, 64, -CH_2-CH-CH_2-), 5.19 (m, 63, -CH_2-CH-CH_2-), 5.48 (s, 64, CH), 7.31 (m, 194, arom. CH), 7.44 (m, 128, arom. CH). ^{13}C NMR ($CDCl_3$): δ 172.28 (COOR), 171.91 (COOR), 171.61 (COOR), 138.08 (CH), 129.25 (CH), 128.47 (CH), 126.23 (CH), 101.24 (CH), 69.47 (CH), 69.12 (CH_2), 66.54 (CH), 62.45 (CH_2), 29.33 (CH_2), 29.17 (CH_2), 29.02 (CH_2), 28.83 (CH_2). MALDI MS 27059 m/z $[M-H]^+$ (Theory: 27500 m/z $[M]^+$). SEC M_w: 16150, M_n: 15870, PDI: 1.02.

Example 25

Syntheses of [Gn]-PGLSA Dendrons with Focal NHS Activated Ester

Example 25.1 Synthesis of [2-(cis-1,3-O-benzylidene glycerol)-N-succinimidyl] succinate (bzld-[G1]-PGLSA-NHS dendron) - 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester (11.47 g, 40.92 mmol), N-hydroxy succinimide (4.85 g,

42.18 mmol), and DPTS (4.26 g, 14.50 mmol), were dissolved in CH_2Cl_2 (100 mL). The reaction flask was flushed with nitrogen and then DCC (13.44 g, 65.14 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. The DCC-urea was filtered and washed with a small amount of CH_2Cl_2 (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. Following vacuum filtration, 13.0 g of a white solid was collected (84 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (broad s, 4, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.85 (m, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.96 (m, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.13 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.27 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.72 (m, 1, -CH_2-C$\underline{H}$-CH_2-), 5.52 (s, 1, C$\underline{H}$), 7.34 (m, 3, arom. C$\underline{H}$), 7.47 (m, 2, arom. C$\underline{H}$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 171.32 ($\underline{C}$OOR), 169.12 ($\underline{C}$OOR), 167.82 ($\underline{C}$OOR), 137.96 ($\underline{C}$H), 129.30 ($\underline{C}$H), 128.51 ($\underline{C}$H), 126.23 ($\underline{C}$H), 101.38 ($\underline{C}$H), 69.11 ($\underline{C}H_2$), 66.94 ($\underline{C}$H), 29.08 ($\underline{C}H_2$), 26.51 ($\underline{C}H_2$), 25.74 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 29318 (aliph. C-H stretch), 1820.09 and 1727 (C=O). GC-MS 378 m/z $[M-H]^+$ (Theory: 377 m/z $[M]^+$). Elemental Analysis C: 57.22 %; H 5.07 % (Theory: C: 57.29 %; H 5.08 %).

Example 25.2 Synthesis of bzld-[G2]-PGLSA-NHS dendron - Pd/C (10% w/w) was added to a solution of bzld-[G1]-PGLSA-NHS dendron (0.514 g, 1.36 mmol) in THF (20 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 20 min. The catalyst and activated carbon were filtered off and washed with THF (50 mL). 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester (0.975 g, 3.48 mmol) and DPTS (0.475 g, 1.61 mmol) were directly added to this solution. The reaction flask was flushed with nitrogen and then DCC (1.08 g, 5.24 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. The DCC-urea was filtered and washed with a small amount of THF (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. Following vacuum filtration, 0.991 g of a white solid was collected (70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (broad s, 4, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.72 (m, 10, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.90 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.14 (m, 6, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.25 (m, 6, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.70 (m, 2, -CH_2-C$\underline{H}$-CH_2-), 5.25 (m, 1, -CH_2-C$\underline{H}$-CH_2-), 5.52 (s, 2, C$\underline{H}$), 7.33 (m, 6, arom. C$\underline{H}$), 7.47 (m, 4, arom. C$\underline{H}$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 172.31 ($\underline{C}$OOR), 171.92 ($\underline{C}$OOR), 170.35 ($\underline{C}$OOR), 169.12

(<u>C</u>OOR), 167.80 (<u>C</u>OOR), 138.02 (<u>C</u>H), 129.27 (<u>C</u>H), 128.49 (<u>C</u>H), 126.21 (<u>C</u>H), 101.33 (<u>C</u>H), 69.97 ($\underline{C}H_2$), 69.17 ($\underline{C}H_2$), 66.53 (<u>C</u>H), 62.49 ($\underline{C}H_2$), 29.38 ($\underline{C}H_2$), 29.05 ($\underline{C}H_2$), 26.35 ($\underline{C}H_2$), 25.74 ($\underline{C}H_2$). FAB MS 814.3 m/z $[M-H]^+$ (Theory: 813.8 m/z $[M]^+$). Elemental Analysis C: 57.42 %; H 5.40 % (Theory: C: 57.56 %; H 5.33 %).

Example 25.3 Synthesis of bzld-[G3]-PGLSA-NHS dendron - Pd/C (10% w/w) was added to a solution of bzld-[G2]-PGLSA-NHS dendron (0.687 g, 0.844 mmol) in THF (20 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 20 min. The catalyst and activated carbon were filtered off and washed with THF (50 mL). 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester (1.269 g, 4.53 mmol) and DPTS (0.657 g, 2.23 mmol) were directly added to this solution. The reaction flask was flushed with nitrogen and then DCC (1.08 g, 5.24 mmol) was added. The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. The DCC-urea was filtered and washed with a small amount of THF (20 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 3:97 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. Following vacuum filtration, 0.796 g of a white solid was collected (72 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (m, 9, -$C\underline{H}_2$-$C\underline{H}_2$-), 2.63 (m, 9, -$C\underline{H}_2$-$C\underline{H}_2$-), 2.74 (m, 12, -$C\underline{H}_2$-$C\underline{H}_2$-), 2.89 (t, 2, -$C\underline{H}_2$-$C\underline{H}_2$-), 4.14 (m, 14, -$C\underline{H}_2$-CH-$C\underline{H}_2$-), 4.24 (m, 14, -$C\underline{H}_2$-CH-$C\underline{H}_2$-), 4.70 (m, 4, -CH_2-C<u>H</u>-CH_2-), 5.20 (m, 2, -CH_2-C<u>H</u>-CH_2-), 5.26 (m, 1, -CH_2-C<u>H</u>-CH_2-), 5.51 (s, 4, C<u>H</u>), 7.33 (m, 12, arom. C<u>H</u>), 7.47 (m, 8, arom. C<u>H</u>). ^{13}C NMR (400 MHz, $CDCl_3$): δ 172.29 (<u>C</u>OOR), 171.92 (<u>C</u>OOR), 171.59 (<u>C</u>OOR), 169.23 (<u>C</u>OOR), 167.87 (<u>C</u>OOR), 138.03 (<u>C</u>H), 129.27 (<u>C</u>H), 128.48 (<u>C</u>H), 126.21 (<u>C</u>H), 101.33 (<u>C</u>H), 69.51 ($\underline{C}H_2$), 69.17 ($\underline{C}H_2$), 66.54 (<u>C</u>H), 62.51 ($\underline{C}H_2$), 29.37 ($\underline{C}H_2$), 29.04 ($\underline{C}H_2$), 28.86 ($\underline{C}H_2$), 25.73 ($\underline{C}H_2$). FAB MS 1686.7 m/z $[M-H]^+$ (Theory: 1686.6 m/z $[M]^+$). Elemental Analysis C: 57.52 %; H 5.53 % (Theory: C: 57.68 %; H 5.44 %).

<u>Example 26</u>

Synthesis of [G2]-PGLSA-(Z)Lys(Z) – Z-Lys(Z)-OH (1.88 g, 4.53 mmol), [G2]-PGLSA (0.401 g, 0.170 mmol), and DPTS (0.66 g, 2.24 mmol) were dissolved in THF (20 mL). The reaction flask was flushed with nitrogen and then DCC (1.43 g, 6.93 mmol) was added. Stirring at room temperature was continued for 24 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (20 mL) and the solvent was evaporated. The crude product was purified by silica gel

chromatography, eluting with 2:98 to 4:96 methanol:CH_2Cl_2. The product was dissolved in CH_2Cl_2, filtered (to remove any DCU), and precipitated in ethyl ether at –20 °C to remove remaining DCC. The ethyl ether was decanted and the precipitate was isolated to yield 1.69 g of a white solid (95.1 % yield). ^1H NMR ($CDCl_3$): δ 1.28 (broad s, 32, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.43 (broad s, 32, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.59 (broad s, 16, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.72 (broad s, 16, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.59 (broad s, 32, $-CH_2-CH_2-CH_2-C\underline{H}_2-NH-$), 2.54 (broad s, 52, $-C\underline{H}_2-C\underline{H}_2-$), 4.09-4.28 (broad m, 23, $-C\underline{H}_2-CH-C\underline{H}_2-$ and -CH2-C$\underline{H}$CO-NH-), 5.00 (s, 32, $-C\underline{H}_2-Ph$), 5.03 (s, 32, $-C\underline{H}_2-Ph$), 5.18 (m, 14, $-CH_2-C\underline{H}-CH_2-$), 7.25 (m, 165, arom. C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 171.98 ($\underline{C}$OOR), 171.51 ($\underline{C}$OOR), 156.80 ($\underline{C}$OOR), 156.34 ($\underline{C}$OOR), 136.84 ($\underline{C}$H), 136.44 ($\underline{C}$H), 128.67 ($\underline{C}$H), 128.29 ($\underline{C}$H), 67.19 ($\underline{C}$H), 66.76 ($\underline{C}$H), 62.58 ($\underline{C}H_2$), 53.96 ($\underline{C}$H), 40.62 ($\underline{C}H_2$), 31.80 ($\underline{C}H_2$) 29.49 ($\underline{C}H_2$), 28.89 ($\underline{C}H_2$), 28.73 ($\underline{C}H_2$), 22.56 ($\underline{C}H_2$). MALDI MS 8708.0 m/z $[M-H]^+$ (Theory: 8699.0 m/z $[M]^+$). SEC M_w: 7330, M_n: 7220, PDI: 1.01.

Example 27

Synthesis of [G2]-PGLSA-Lys – [G2]-PGLSA-Z-Lys(Z) (59.0 mg, 0.00678 mmol), was dissolved in DMF (3 mL). The reaction flask was flushed with nitrogen and then 10% Pd/C (400 mg) was added and stirred vigorously. To this stirring solution, formic acid was slowly added via syringe. The solution began to bubble and give off heat. Stirring at room temperature was continued for 14 hours under nitrogen atmosphere. Upon completion, Pd/C was filtered and washed with a small amount of 1 N HCl (10 mL), which was added to the DMF solution containing the dendrimer. The resulting solution was added drip wise into a large excess of acetone. The contents were cooled to –20 °C over night. The acetone was decanted and the precipitate was isolated to yield 29.0 mg of product (96.3 % yield). ^1H NMR ($CDCl_3$): δ 1.39 (broad m, 32, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.60 (broad m, 32, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.83 (broad m, 16, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 1.92 (broad m, 16, $-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_2-NH-$), 2.53-2.60 (broad m, 52, $-C\underline{H}_2-C\underline{H}_2-$), 2.87 (broad m, 32, $-CH_2-CH_2-CH_2-C\underline{H}_2-NH-$), 4.08 (broad m, 20, $-C\underline{H}_2-CH-C\underline{H}_2-$ and -CH2-C$\underline{H}$CO-NH-), 4.09 (broad m, 23, $-C\underline{H}_2-CH-C\underline{H}_2-$ and -CH2-C$\underline{H}$CO-NH-), 4.21 (broad m, 25, $-C\underline{H}_2-CH-C\underline{H}_2-$ and -CH2-C$\underline{H}$CO-NH-), 4.35 (broad m, 16, $-C\underline{H}_2-CH-C\underline{H}_2-$ and -CH2-C$\underline{H}$CO-NH-), 4.43 (broad m, 16, $-C\underline{H}_2-CH-C\underline{H}_2-$ and -CH2-C$\underline{H}$CO-NH-), 5.19 (m, 5, $-CH_2-C\underline{H}-CH_2-$), 5.30 (m, 8, $-CH_2-C\underline{H}-CH_2-$). ^{13}C NMR ($CDCl_3$): δ 174.35 ($\underline{C}$OOR), 173.74 ($\underline{C}$OOR), 169.67 ($\underline{C}$OOR), 70.04 ($\underline{C}$H), 64.21 ($\underline{C}H_2$), 63.01 ($\underline{C}H_2$), 52.72 ($\underline{C}H_2$), 39.17 ($\underline{C}H_2$), 37.07 ($\underline{C}H_2$),

29.38 ($\underline{C}H_2$) 28.81 ($\underline{C}H_2$), 26.44 ($\underline{C}H_2$), 21.78 ($\underline{C}H_2$), 21.71 ($\underline{C}H_2$). MALDI MS 4404 m/z $[M-H]^+$ (Theory: 4407 m/z $[M]^+$). SEC M_w: 7730, M_n: 7580, PDI: 1.02.

Example 28

Synthesis of [G2]-PGLSA-COOH - [G2]-PGLSA-OH (0.636 g, 0.270 mmol) was dissolved in pyridine (20 mL) and stirred while succinic anhydride (0.649 g, 6.485 mmol) was added. The reaction mixture was stirred for 16 hours at 35 oC before the pyridine was removed under reduced pressure. The contents were partially dissolved in DCM (15 mL), and 0.1 N HCl (15 mL) was then added and the mixture was stirred for an additional 15 minutes. After stirring, the organic and aqueous phases separated and a layer was formed between the two phases. While avoiding the interface, most of the aqueous and organic phases were removed. This washing procedure with 15 mL of DCM and 0.1 N HCl was repeated two more times. Any remaining organic or aqueous phase was removed first by rotoevaporation followed by lyopholization to yield 0.990 g of a highly viscous liquid (92.7 % yield). MALDI MS 3958.4 m/z $[M+H]^+$, (Theory: 3957.2 m/z $[M]^+$).

Example 29

Synthesis of [G4]-PGLSA-COOH and [G4]-PGLSA-COO^-Na^+ - [G4]-PGLSA-OH (0.140 g, 0.0131 mmol) was dissolved in pyridine (10 mL) and stirred while succinic anhydride (0.167 g, 1.68 mmol) was added. The reaction mixture was stirred for 16 hours before the pyridine was removed under reduced pressure. The contents were partially dissolved in DCM (15 mL), and 0.1 N HCl (15 mL) was then added and the mixture was stirred for an additional 15 minutes. After stirring, the organic and aqueous phases separated and a layer was formed between the two phases. While avoiding the interface, most of the aqueous and organic phases were removed. This washing procedure with 15 mL of DCM and 0.1 N HCl was repeated two more times. Any remaining organic or aqueous phase was removed first by rotoevaporation followed by lyopholization to yield 0.191 g of a highly viscous liquid (85 % yield). To dissolve the polymer in water, deionized water (10 mL) and brine (0.5 mL) were added to the solution and 0.05 N NaOH was added drop-wise to the stirring solution until the pH remained at 7.0. The dendrimer was purified via dialysis with 7,000 MW cutoff dialysis tubing for 24 hours in DI water. The water was then removed via lyopholization to obtain a white solid. ^{1}H NMR (D_2O): δ 2.32 (m, 130, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.46 (m, 133, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.58 (m, 228, -C$\underline{H}_2$-C$\underline{H}_2$-) 4.13-4.21 (m, 240, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 5.18 (m, 62, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR (D_2O): δ 180.72 ($\underline{C}$OOH), 175.37 ($\underline{C}$OOH), 173.52 ($\underline{C}$OOR), 70.14 ($\underline{C}$H), 69.76 ($\underline{C}$H), 62.80 ($\underline{C}H_2$), 34.31 ($\underline{C}H_2$), 32.10 ($\underline{C}H_2$), 30.72

($\underline{C}H_2$), 29.01 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 3368 (OH), 2964 (aliph. C-H stretch), 1732 (C=O), 1567 (asym COO^- stretch), 1409 (sym COO^- stretch), 1149 (C-O stretch). MALDI MS 17168 m/z $[M + Na]^+$, 8602 m/z $[M + Na]^{2+}$, (Theory: 17120.0 m/z $[M]^+$). SEC M_w: 8330, M_n: 7780, PDI: 1.11.

Example 30

Synthesis of 2-(tert-Butyldiphenylsilanyloxy)-succinic acid 4-(2-phenyl-[1,3]dioxan-5-yl) ester – L-Malic acid (2.00 g, 15.0 mmol) was dissolved in pyridine (25 mL) and *tert*-butylchlorodiphenylsilane (3.9 mL, 15.0 mmol) was added via syringe. The reaction was stirred for 14 hours before the pyridine was removed by vacuum. The remaining residue was dissolved in DCM (100 mL) and washed with 0.2 N HCl (2x 100 mL). The organic layer was dried with Na_2SO_4, filtered, and evaporated. Crude 2-(*tert*-butyldiphenylsilanyloxy) succinic acid was subsequently dissolved in a 2:1 mixture of trifluoroacetic anhydride and THF (50 mL) respectively and heated to 50 °C for 2 hours. The solvents were removed by vacuum and the crude mixture was azeotroped with toluene. The crude anhydride was dissolved in pyridine and *cis*-1,3-*O*-benzylideneglycerol (2.7 g, 54.9 mmol) was added before the solution was stirred another 14 hours. The pyridine was removed by vacuum. The remaining residue was dissolved in DCM (100 mL) and washed with 0.2 N HCl (2x 100 mL). The organic layer was dried with Na_2SO_4, filtered, and evaporated. The crude product was purified by silica gel chromatography, eluting with 79:20:1 to 59:40:1 hexane: ethyl acetate: acetic acid. 0.99 g of a viscous clear liquid were isolated following evaporation of solvents (90 % yield) evaporated to give 1.18 g of a clear viscous oil (12.3% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 9, -$C\underline{H}_3$), 2.78 (broad m, 2, -$C\underline{H}_2$-CH-), 3.64 (broad m, 4, -$C\underline{H}_2$-CH-$C\underline{H}_2$-), 4.87 (m, 1, -CH_2-C$\underline{H}$-CH_2-) 2.78 (t, 1, -CH_2-C$\underline{H}$-), 5.50 (s, 1, C$\underline{H}$), 7.34 (broad m, 4, arom. C$\underline{H}$), 7.48 (broad m, 11, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 177.54 ($\underline{C}$OOH), 175.91 ($\underline{C}$OOH), 171.63 ($\underline{C}$OOR), 138.00 ($\underline{C}$H), 136.20 ($\underline{C}$H), 136.14 ($\underline{C}$H), 132.94 ($\underline{C}$H), 130.20 ($\underline{C}$H), 129.25 ($\underline{C}$H), 128.41 ($\underline{C}$H), 127.95 ($\underline{C}$H), 127.81 ($\underline{C}$H), 126.35 ($\underline{C}$H), 101.41 ($\underline{C}$H), 69.43 ($\underline{C}H_2$), 68.78 ($\underline{C}$H), 66.91 ($\underline{C}H_2$), 39.92 ($\underline{C}$H), 26.99 ($\underline{C}H_3$), 20.95 ($\underline{C}$H), 19.53 ($\underline{C}H_2$). FAB-MS 535.2 m/z $[M+H]^+$ (Theory: 534.67 m/z $[M]^+$).

Example 31

Synthesis of [G0]-PGLAA-bzld - Adipic acid (6.474 g, 44.300 mmol), *cis*-1,3-*O*-benzylideneglycerol (17.571 g, 97.508 mmol), and DPTS (10.01 g, 34.03 mmol) were dissolved in DCM (120 mL) followed by the addition of DCC (28.260 g, 136.96 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon reaction completion, the DCC-urea was filtered and washed with a small amount of DCM (50 mL). The crude product was purified by silica gel chromatography, eluting with 2% MeOH in DCM. The appropriate isolated fractions were concentrated, filtered (to remove any DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. Following vacuum filtration, 12.694 g of a white solid was collected (60.8 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (s, 4, -CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-), 2.45 (s, 4, -C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-), 4.12 (m, 4, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.25 (m, 4, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.68 (m, 2, -CH_2-C$\underline{H}$-CH_2-), 5.52 (s, 2, C$\underline{H}$), 7.34 (m, 6, arom. C$\underline{H}$), 7.48 (m, 4, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.47 ($\underline{C}$OOR), 138.01 ($\underline{C}$H), 129.27 ($\underline{C}$H), 128.50 ($\underline{C}$H), 126.22 ($\underline{C}$H), 101.43 ($\underline{C}$H), 69.30 ($\underline{C}H_2$), 66.08 ($\underline{C}$H), 34.15 ($\underline{C}H_2$), 24.49 ($\underline{C}H_2$). FAB 471.2 m/z $[M+H]^+$ (Theory: 470.51 m/z $[M]^+$).

Example 32

Synthesis of [G0]-PGLAA-OH - $Pd(OH)_2$/C (10% w/w) was added to a solution of [G0]-PGLAA-bzld (2.161 g, 4.593 mmol) in THF (30 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF solution (50 mL). The filtrate was evaporated to give 1.303 g of a clear viscous oil (96.4 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 1.64 (m, 4, -CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-), 2.36 (m, 4, -C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-), 3.51 (m, 1, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 3.64 (m, 5, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 3.78 (m, 1, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.03 (m, 1, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.12 (m, 1, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.76 ($\underline{C}$OOR), 75.43 ($\underline{C}$H), 69.91 ($\underline{C}$H), 65.33 ($\underline{C}H_2$), 62.83 ($\underline{C}H_2$), 60.49 ($\underline{C}H_2$), 33.52 ($\underline{C}H_2$), 33.31 ($\underline{C}H_2$), 24.12 ($\underline{C}H_2$). FAB MS 295.30 m/z $[M+H]^+$ (Theory: 294.30 m/z $[M]^+$).

Example 33

Synthesis of adipic anhydride – Adipic acid (96.28 g, 0.6588mol) and acetic anhydride (400 mL) were combined and refluxed at 160 °C for four hours. Afterwards, the acetic acid/anhydride was removed under vacuum. Next the depolymerization catalyst, zinc acetate monohydrate, was added along with a distillation apparatus and the heat was slowly

increased. After 100 °C, nothing was collected until 200 °C when 68.79 g of a clear colorless liquid was collected (82.5 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (m, 4, -CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-), 2.67 (m, 4, -C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.38 (-$\underline{C}$OOCO-), 34.60 ($\underline{C}H_2$), 22.37 ($\underline{C}H_2$). GC-MS 128 m/z $[M]^+$ (Theory: 128.12 m/z $[M]^+$).

Example 34

Synthesis of 2-(*cis*-1,3-*O*-benzylidene glycerol)adipic acid mono ester

cis-1,3-*O*-benzylideneglycerol (68.74 g, 0.5365 mol) was dissolved in pyridine (150 mL) followed by the addition of adipic anhydride (82.50 g, 0.4578 mol). The reaction mixture was stirred at room temperature for 18 hours before the pyridine was removed under vacuum at 35 °C. The remaining solid was dissolved in DCM (400 mL) and washed two times with 0.2 N HCl (400 mL), or until the aqueous phase remained at pH 1. The organic phase was evaporated and the solid was added to deionized water (300 mL). 1 N NaOH was added until pH 7 was obtained and the product was in the aqueous solution. The aqueous phase was washed with DCM (400 mL), to extract any remaining adipic anhydride, and then readjusted to pH 4. The aqueous phase was subsequently extracted twice with DCM (400 mL), dried with Na_2SO_4, filtered, and evaporated to afford 67.53 g of a white powder (47.80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (m, 4, -CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-), 2.35 (m, 2, -C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-), 2.44 (m, 2, -C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-), 4.13 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.25 (m, 2, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.67 (m, 1, -CH_2-C$\underline{H}$-CH_2-), 5.53 (s, 1, C$\underline{H}$), 7.33 (m, 3, arom. C$\underline{H}$), 7.47 (m, 2, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 178.98 ($\underline{C}$OOH), 173.48 ($\underline{C}$OOR), 137.97 ($\underline{C}$H), 129.30 ($\underline{C}$H), 128.51 ($\underline{C}$H), 126.22 ($\underline{C}$H), 101.45 ($\underline{C}$H), 69.28 ($\underline{C}H_2$), 66.13 ($\underline{C}$H), 34.13 ($\underline{C}H_2$), 33.71 ($\underline{C}H_2$), 24.43 ($\underline{C}H_2$), 24.21 ($\underline{C}H_2$). FAB MS 309.1 m/z (MH^+) (Theory: 308.33 m/z (M^+)).

Example 35

Synthesis of [G1]-PGLAA-bzld - First, 2-(*cis*-1,3-*O*-benzylidene glycerol)adipic acid mono ester (7.226 g, 23.434 mmol), [G0]-PGLAA-OH (1.222 g, 4.152 mmol), and DPTS (2.830 g, 9.621 mmol) were dissolved in THF (100 mL) followed by the addition of DCC (4.32 g, 21.0 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon reaction completion, the DCC-urea was filtered and washed with a small amount of THF (50 mL). The crude product was purified by silica gel

chromatography, eluting with 1/1 to 4/1 EtOAc:hexanes. The appropriate isolated fractions were concentrated, filtered (to remove any DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 5.99 g of a sticky solid (99.1 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (m, 20, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.32 (m, 12, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.43 (m, 8, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 4.10 (m, 12, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.25 (m, 12, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.68 (m, 4, $-CH_2-C\underline{H}-CH_2-$), 5.21 (m, 2, $-CH_2-C\underline{H}-CH_2-$), 5.51 (s, 4, $C\underline{H}$), 7.32 (m, 12, arom. $C\underline{H}$), 7.47 (m, 8, arom. $C\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.40 ($\underline{C}OOR$), 172.87 ($\underline{C}OOR$), 172.55 ($\underline{C}OOR$), 138.02 ($\underline{C}H$), 129.28 ($\underline{C}H$), 128.49 ($\underline{C}H$), 126.21 ($\underline{C}H$), 101.39 ($\underline{C}H$), 69.28 ($\underline{C}H_2$), 66.11 ($\underline{C}H$), 62.39 ($\underline{C}H_2$), 34.08 ($\underline{C}H_2$), 33.90 ($\underline{C}H_2$), 33.75 ($\underline{C}H_2$), 24.37 ($\underline{C}H_2$). FAB MS 1455.6 m/z $[M+H]^+$ (Theory: 1455.54 m/z $[M]^+$).

Example 36

Synthesis of [G1]-PGLAA-OH - $Pd(OH)_2/C$ (10% w/w) was added to a solution of [G1]-PGLAA-bzld (4.870 g, 3.346 mmol) in THF (50 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF solution (50 mL). The filtrate was evaporated to give 3.669 g of a clear viscous oil (99.5 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 1.63 (m, 20, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.36 (m, 20, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 3.52 (m, 2, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.59-3.69 (broad m, 12, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.79 (m, 1, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.03 (m, 1, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.14 (m, 5, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.32 (m, 4, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 5.24 (m, 2, $-CH_2-C\underline{H}-CH_2-$). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.64 ($\underline{C}OOR$), 173.36 ($\underline{C}OOR$), 172.93 ($\underline{C}OOR$), 75.42 ($\underline{C}H$), 69.93 ($\underline{C}H$), 69.47 ($\underline{C}H$), 65.36 ($\underline{C}H_2$), 62.87 ($\underline{C}H_2$), 62.15 ($\underline{C}H_2$), 60.50 ($\underline{C}H_2$), 33.49 ($\underline{C}H_2$), 33.35 ($\underline{C}H_2$), 33.20 ($\underline{C}H_2$), 24.11 ($\underline{C}H_2$). MALDI-TOF MS 1125.8 m/z $[M+Na]^+$ (Theory: 1103.11 m/z $[M]^+$).

Example 37

Synthesis of [G2]-PGLAA-bzld - 2-(*cis*-1,3-*O*-benzylidene glycerol)adipic acid mono ester (10.012 g, 32.472 mmol), [G1]-PGLAA-OH (3.397 g, 3.079 mmol), and DPTS (2.508 g, 8.527 mmol) were dissolved in THF (100 mL) followed by the addition of DCC (4.62 g, 22.4 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon reaction completion, the DCC-urea was filtered and washed with a small amount of THF (50 mL). The crude product was purified by silica gel chromatography,

eluting with 2% MeOH in DCM. The appropriate isolated fractions were concentrated, filtered (to remove any DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 9.39 g of a sticky wax (89.0 % yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.63 (m, 52, -CH$_2$-C$\underline{H}_2$-C$\underline{H}_2$-CH$_2$-), 2.31 (m, 36, -C$\underline{H}_2$-CH$_2$-CH$_2$-C$\underline{H}_2$-), 2.41 (m, 16, -C$\underline{H}_2$-CH$_2$-CH$_2$-C$\underline{H}_2$-), 4.05 (m, 28, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.25 (m, 28, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.67 (m, 8, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.21 (m, 6, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.51 (s, 8, C$\underline{H}$), 7.33 (m, 24, arom. C$\underline{H}$), 7.46 (m, 16, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 173.39 ($\underline{C}$OOR), 172.87 ($\underline{C}$OOR), 172.54 ($\underline{C}$OOR), 138.02 ($\underline{C}$H), 129.27 ($\underline{C}$H), 128.49 ($\underline{C}$H), 126.21 ($\underline{C}$H), 101.38 ($\underline{C}$H), 69.27 ($\underline{C}$H$_2$), 66.11 ($\underline{C}$H), 62.39 ($\underline{C}$H$_2$), 34.08 ($\underline{C}$H$_2$), 33.74 ($\underline{C}$H$_2$), 33.67 ($\underline{C}$H$_2$), 24.37 ($\underline{C}$H$_2$). MALDI MS 3449.2 m/z [M+Na]$^+$ (Theory: 3425.61 m/z [M]$^+$).

Example 38

Synthesis of [G2]-PGLAA-OH - Pd(OH)$_2$/C (10% w/w) was added to a solution of [G2]-PGLAA-bzld (8.02 g, 2.34 mmol) in THF (100 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H$_2$ before shaking for 10 hours. The catalyst was filtered and washed with THF solution (50 mL). The filtrate was evaporated to give 6.360 g of a clear viscous oil (99.4 % yield). ^{1}H NMR (400 MHz, CD$_3$OD): δ 1.62 (m, 52, -CH$_2$-C$\underline{H}_2$-C$\underline{H}_2$-CH$_2$-), 2.35 (m, 52, -C$\underline{H}_2$-CH$_2$-CH$_2$-C$\underline{H}_2$-), 3.52 (m, 5, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 3.59-3.71 (broad m, 25, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 3.79 (m, 3, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.03 (m, 3, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.14 (m, 15, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.33 (m, 12, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 5.25 (m, 6, -CH$_2$-C$\underline{H}$-CH$_2$-). ^{13}C NMR (100.6 MHz, CD$_3$OD): δ 173.63 ($\underline{C}$OOR), 173.27 ($\underline{C}$OOR), 172.92 ($\underline{C}$OOR), 75.42 ($\underline{C}$H), 69.94 ($\underline{C}$H), 69.47 ($\underline{C}$H), 65.38 ($\underline{C}$H$_2$), 62.89 ($\underline{C}$H$_2$), 62.17 ($\underline{C}$H$_2$), 60.52 ($\underline{C}$H$_2$), 33.51 ($\underline{C}$H$_2$), 33.39 ($\underline{C}$H$_2$), 33.22 ($\underline{C}$H$_2$), 24.12 ($\underline{C}$H$_2$). MALDI-TOF MS 2744.3 m/z [M+Na]$^+$ (Theory: 2720.75 m/z [M]$^+$).

Example 39

Synthesis of [G3]-PGLAA-bzld - 2-(*cis*-1,3-*O*-benzylidene glycerol)adipic acid mono ester (12.626 g, 40.950 mmol), [G2]-PGLAA-OH (5.263 g, 1.934 mmol), and DPTS (3.232 g, 10.989 mmol) were dissolved in THF (100 mL) followed by the addition of DCC (12.581 g, 60.975 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon reaction completion, the DCC-urea was filtered and washed with a small amount of THF (60 mL). The crude product was purified by silica gel chromatography,

eluting with 1.5 to 3.0 % MeOH in DCM. The appropriate isolated fractions were concentrated, filtered (to remove any DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 12.22 g of a sticky wax (85.8 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (broad m, 130, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.31 (m, 90, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.41 (m, 32, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 4.10 (m, 62, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.24 (m, 62, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.67 (m, 16, $-CH_2-C\underline{H}-CH_2-$), 5.19 (m, 14, $-CH_2-C\underline{H}-CH_2-$), 5.51 (s, 16, $C\underline{H}$), 7.32 (m, 48, arom. $C\underline{H}$), 7.46 (m, 32, arom. $C\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.38 ($\underline{C}OOR$), 172.89 ($\underline{C}OOR$), 172.48 ($\underline{C}OOR$), 138.03 ($\underline{C}H$), 129.27 ($\underline{C}H$), 128.49 ($\underline{C}H$), 126.21 ($\underline{C}H$), 101.36 ($\underline{C}H$), 69.26 ($\underline{C}H_2$), 66.11 ($\underline{C}H$), 62.29 ($\underline{C}H_2$), 34.08 ($\underline{C}H_2$), 33.83 ($\underline{C}H_2$), 33.74 ($\underline{C}H_2$), 33.67 ($\underline{C}H_2$), 24.43 ($\underline{C}H_2$), 24.36 ($\underline{C}H_2$). MALDI-TOF MS 7390 m/z $[M+Na]^+$ (Theory: 7365.73 m/z $[M]^+$).

Example 40

Synthesis of [G3]-PGLAA-OH - $Pd(OH)_2/C$ (10% w/w) was added to a solution of [G3]-PGLAA-bzld (11.03 g, 1.497 mmol) in THF (125 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF solution (75 mL). The filtrate was evaporated to give 8.69 g of a clear viscous oil (97.5 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 1.63 (m, 124, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.35 (m, 127, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 3.52 (m, 7, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.60-3.71 (broad m, 55, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.79 (m, 4, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.04 (m, 5, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.14 (m, 34, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.32 (m, 29, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 5.25 (m, 14, $-CH_2-C\underline{H}-CH_2-$). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.82 ($\underline{C}OOR$), 173.63 ($\underline{C}OOR$), 173.36 ($\underline{C}OOR$), 173.27 ($\underline{C}OOR$), 172.92 ($\underline{C}OOR$), 75.45 ($\underline{C}H$), 75.40 ($\underline{C}H$), 69.96 ($\underline{C}H$), 69.48 ($\underline{C}H$), 65.40 ($\underline{C}H_2$), 62.92 ($\underline{C}H_2$), 62.23 ($\underline{C}H_2$), 60.54 ($\underline{C}H_2$), 33.53 ($\underline{C}H_2$), 33.25 ($\underline{C}H_2$), 24.15 ($\underline{C}H_2$). MALDI-TOF MS 5975.0 m/z $[M+Na]^+$ (Theory: 5956.02 m/z $[M]^+$).

Example 41

Synthesis of [G0]-PGLSA-[G1]-PGLAA-bzld - 2-(*cis*-1,3-*O*-benzylidene glycerol)adipic acid mono ester (11.793 g, 38.248 mmol), [G0]-PGLSA-OH (1.185 g, 4.449 mmol), and DPTS (2.853 g, 9.700 mmol) were dissolved in THF (50 mL) followed by the addition of DCC (7.216 g, 34.973 mmol). The reaction was stirred at room temperature for 14 hours

under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (50 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 1/1 to 4/1 EtOAc:hexanes. The appropriate isolated fractions were concentrated, filtered (to remove any remaining DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 7.173 g of a sticky solid (97 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65 (m, 16, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.33 (m, 8, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.42 (m, 8, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.59 (m, 4, $-C\underline{H}_2-C\underline{H}_2-$), 4.11 (m, 12, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.24 (m, 12, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.67 (m, 4, $-CH_2-C\underline{H}-CH_2-$), 5.20 (m, 2, $-CH_2-C\underline{H}-CH_2-$), 5.51 (s, 4, C$\underline{H}$), 7.33 (m, 12, arom. C$\underline{H}$), 7.47 (m, 8, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.41 ($\underline{C}$OOR), 172.92 ($\underline{C}$OOR), 171.48 ($\underline{C}$OOR), 138.02 ($\underline{C}$H), 129.28 ($\underline{C}$H), 128.49 ($\underline{C}$H), 126.21 ($\underline{C}$H), 101.38 ($\underline{C}$H), 69.65 ($\underline{C}$H), 69.27 ($\underline{C}H_2$), 66.11 ($\underline{C}$H), 62.19 ($\underline{C}H_2$), 34.09 ($\underline{C}H_2$), 33.73 ($\underline{C}H_2$), 28.97 ($\underline{C}H_2$), 24.44 ($\underline{C}H_2$), 24.36 ($\underline{C}H_2$). FAB MS 1425.5 m/z $[M+H]^+$ (Theory: 1427.49 m/z $[M]^+$). SEC M_w: 1670, M_n: 1650, PDI: 1.01.

Example 42

Synthesis of [G0]-PGLSA-[G1]-PGLAA-OH - $Pd(OH)_2/C$ (10% w/w) was added to a solution of [G0]-PGLSA-[G1]-PGLAA-bzld (5.900 g, 4.133 mmol) in THF (50 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF (50 mL). The filtrate was evaporated to give 4.407 g of a colorless, viscous oil (99 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 1.63 (m, 16, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.36 (m, 16, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.61 (m, 4, $-C\underline{H}_2-C\underline{H}_2-$), 3.52 (m, 3, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.59-3.65 (broad m, 9, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.69 (m, 2, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.79 (m, 2, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.03 (m, 2, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.15 (m, 5, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.30 (m, 4, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 5.25 (m, 2, $-CH_2-C\underline{H}-CH_2-$). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.85 ($\underline{C}$OOR), 173.67 ($\underline{C}$OOR), 173.41 ($\underline{C}$OOR), 171.95 ($\underline{C}$OOR), 75.42 ($\underline{C}$H), 69.93 ($\underline{C}$H), 69.78 ($\underline{C}$H), 65.36 ($\underline{C}H_2$), 62.87 ($\underline{C}H_2$), 62.04 ($\underline{C}H_2$), 60.50 ($\underline{C}H_2$), 33.50 ($\underline{C}H_2$), 33.29 ($\underline{C}H_2$), 33.19 ($\underline{C}H_2$), 28.61 ($\underline{C}H_2$), 24.12 ($\underline{C}H_2$). MALDI-TOF MS 1097.5 m/z $[M+Na]^+$ (Theory: 1075.06 m/z $[M]^+$). SEC M_w: 1680, M_n: 1660, PDI: 1.01.

Example 43

Synthesis of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-bzld - 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester (12.758 g, 45.520 mmol), [G0]-PGLSA-[G1]-PGLAA-OH (4.284 g, 3.984 mmol), and DPTS (5.112 g, 17.381 mmol) were dissolved in THF (100 mL) followed by the addition of DCC (13.912 g, 67.436 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (50 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 2% MeOH in DCM. The appropriate isolated fractions were concentrated, filtered (to remove any remaining DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 10.84 g of a white solid (85.7 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (m, 17, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.30 (m, 17, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.63 (m, 20, $-C\underline{H}_2-C\underline{H}_2-$), 2.72 (m, 16, $-C\underline{H}_2-C\underline{H}_2-$), 4.11 (m, 29, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.23 (m, 29, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.70 (m, 8, $-CH_2-C\underline{H}-CH_2-$), 5.20 (m, 6, $-CH_2-C\underline{H}-CH_2-$), 5.51 (s, 8, C$\underline{H}$), 7.34 (m, 12, arom. C$\underline{H}$), 7.46 (m, 8, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.41 ($\underline{C}$OOR), 172.92 ($\underline{C}$OOR), 171.48 ($\underline{C}$OOR), 138.02 ($\underline{C}$H), 129.28 ($\underline{C}$H), 128.49 ($\underline{C}$H), 126.21 ($\underline{C}$H), 101.38 ($\underline{C}$H), 69.65 ($\underline{C}$H), 69.27 ($\underline{C}H_2$), 66.11 ($\underline{C}$H), 62.19 ($\underline{C}H_2$), 34.09 ($\underline{C}H_2$), 33.73 ($\underline{C}H_2$), 28.97 ($\underline{C}H_2$), 24.44 ($\underline{C}H_2$), 24.36 ($\underline{C}H_2$). MALDI-TOF MS 3172.7 m/z $[M+Na]^+$ (Theory: 3173.13 m/z $[M]^+$). SEC M_w: 3600, M_n: 3540, PDI: 1.02.

Example 44

Synthesis of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-OH - $Pd(OH)_2$/C (10% w/w) was added to a solution of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-bzld (5.251 g, 1.655 mmol) in THF (100 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF (50 mL). The filtrate was evaporated to give 4.011 g of a colorless, viscous oil (98.2 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 1.62 (m, 17, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.36 (m, 17, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.64 (m, 36, $-C\underline{H}_2-C\underline{H}_2-$), 3.52 (m, 2, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.60-3.66 (broad m, 26, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.69 (m, 9, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 3.80 (m, 1, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.18 (m, 14, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 4.32 (m, 12, $-C\underline{H}_2-C\underline{H}-C\underline{H}_2-$), 5.25 (m, 6, $-CH_2-C\underline{H}-CH_2-$). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.38 ($\underline{C}$OOR), 173.05 ($\underline{C}$OOR), 172.56 ($\underline{C}$OOR), 172.24 ($\underline{C}$OOR), 172.00 ($\underline{C}$OOR), 75.81 ($\underline{C}$H), 69.80 ($\underline{C}$H), 69.35 ($\underline{C}$H), 67.65 ($\underline{C}H_2$), 65.68 ($\underline{C}H_2$), 62.87 ($\underline{C}H_2$), 62.42 ($\underline{C}H_2$), 62.11 ($\underline{C}H_2$), 60.43 ($\underline{C}H_2$), 33.49 ($\underline{C}H_2$), 33.20 ($\underline{C}H_2$),

28.83 ($\underline{C}H_2$), 28.64 ($\underline{C}H_2$), 25.28 ($\underline{C}H_2$), 24.09 ($\underline{C}H_2$). MALDI-TOF MS 2492.0 m/z $[M+Na]^+$ (Theory: 2468.27 m/z $[M]^+$). SEC M_w: 3390, M_n: 3340, PDI: 1.02.

Example 45

Synthesis of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-bzld - 2-(*cis*-1,3-*O*-benzylidene glycerol)adipic acid mono ester (10.751 g, 34.869 mmol), [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-OH (3.771 g, 1.528 mmol), and DPTS (1.463 g, 4.975 mmol) were dissolved in THF (120 mL) followed by the addition of DCC (10.598 g, 51.365 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (50 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 1.5% MeOH in DCM. The appropriate isolated fractions were concentrated, filtered (to remove any remaining DCU), and directly precipitated in hexanes and cooled to –20 °C overnight. The hexanes were decanted and the precipitate was isolated to yield 9.88 g of a sticky solid (90.9 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (m, 81, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.31 (m, 52, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.42 (m, 32, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.58 (m, 36 $-C\underline{H}_2-C\underline{H}_2-$), 4.10 (m, 62, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.23 (m, 62, $-C\underline{H}_2-CH-C\underline{H}_2-$), 4.66 (m, 16, $-CH_2-C\underline{H}-CH_2-$), 5.19 (m, 14, $-CH_2-C\underline{H}-CH_2-$), 5.51 (s, 16, $C\underline{H}$), 7.33 (m, 47, arom. $C\underline{H}$), 7.46 (m, 32, arom. $C\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.39 ($\underline{C}OOR$), 172.90 ($\underline{C}OOR$), 171.82 ($\underline{C}OOR$), 171.53 ($\underline{C}OOR$), 138.04 ($\underline{C}H$), 129.26 ($\underline{C}H$), 128.49 ($\underline{C}H$), 126.22 ($\underline{C}H$), 101.36 ($\underline{C}H$), 69.65 ($\underline{C}H$), 69.26 ($\underline{C}H_2$), 66.11 ($\underline{C}H$), 62.64 ($\underline{C}H_2$), 62.15 ($\underline{C}H_2$), 34.07 ($\underline{C}H_2$), 33.73 ($\underline{C}H_2$), 28.96 ($\underline{C}H_2$), 28.80 ($\underline{C}H_2$), 24.43 ($\underline{C}H_2$), 24.35 ($\underline{C}H_2$). MALDI-TOF MS 7137.3 m/z $[M+Na]^+$ (Theory: 7113.25 m/z $[M]^+$). SEC M_w: 7160, M_n: 7060, PDI: 1.01.

Example 46

Synthesis of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-OH - $Pd(OH)_2/C$ (10% w/w) was added to a solution of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-bzld (9.175 g, 1.290 mmol) in THF (100 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 10 hours. The catalyst was filtered and washed with THF (50 mL). The filtrate was evaporated to give 7.218 g of a colorless, viscous oil (98.1 % yield). ^1H NMR (400 MHz, CD_3OD): δ 1.63 (m, 83, $-CH_2-C\underline{H}_2-C\underline{H}_2-CH_2-$), 2.37 (m, 83, $-C\underline{H}_2-CH_2-CH_2-C\underline{H}_2-$), 2.61 (m, 36, $-C\underline{H}_2-C\underline{H}_2-$),

3.52 (m, 8, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 3.60-3.71 (broad m, 57, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 3.80 (m, 4, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.03 (m, 5, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.11-4.23 (m, 34, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.30 (m, 29, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 5.25 (m, 14, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.85 ($\underline{C}$OOR), 173.67 ($\underline{C}$OOR), 173.41 ($\underline{C}$OOR), 171.95 ($\underline{C}$OOR), 75.42 ($\underline{C}$H), 69.93 ($\underline{C}$H), 69.78 ($\underline{C}$H), 65.36 ($\underline{C}H_2$), 62.87 ($\underline{C}H_2$), 62.04 ($\underline{C}H_2$), 60.50 ($\underline{C}H_2$), 33.50 ($\underline{C}H_2$), 33.29 ($\underline{C}H_2$), 33.19 ($\underline{C}H_2$), 28.61 ($\underline{C}H_2$), 24.12 ($\underline{C}H_2$). MALDI-TOF MS 5730.3 m/z $[M+Na]^+$ (Theory: 5703.54 m/z $[M]^+$). SEC M_w: 6570, M_n: 6490, PDI: 1.01.

Example 47

Synthesis of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-[G4]-PGLSA-bzld - 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester (11.572 g, 41.286 mmol), [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-OH (5.593 g, 0.981 mmol), and DPTS (4.094 g, 13.919 mmol) were dissolved in THF (80 mL) followed by the addition of DCC (12.596 g, 61.048 mmol). The reaction was stirred at room temperature for 14 hours under nitrogen atmosphere. Upon completion, the DCC-urea was filtered and washed with a small amount of THF (50 mL) and the solvent was evaporated. The crude product was purified by silica gel chromatography, eluting with 1.5% to 5.0% MeOH in DCM. The appropriate isolated fractions were concentrated, filtered (to remove any remaining DCU), and directly precipitated in hexanes and cooled to –20 °C over 48 hours. The hexanes were decanted and the precipitate was isolated to yield 11.50 g of a white solid (83.2 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (m, 83, -CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-), 2.30 (m, 83, -C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-), 2.62 (m, 104, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.70 (m, 63, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.12 (m, 130, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.22 (m, 130, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.68 (m, 32, -CH_2-C$\underline{H}$-CH_2-), 5.18 (m, 30, -CH_2-C$\underline{H}$-CH_2-), 5.50 (s, 32, C$\underline{H}$), 7.33 (m, 97, arom. C$\underline{H}$), 7.46 (m, 66, arom. C$\underline{H}$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172.88 ($\underline{C}$OOR), 172.53 ($\underline{C}$OOR), 172.25 ($\underline{C}$OOR), 171.89 ($\underline{C}$OOR), 138.04 ($\underline{C}$H), 129.26 ($\underline{C}$H), 128.48 ($\underline{C}$H), 126.22 ($\underline{C}$H), 101.28 ($\underline{C}$H), 69.14 ($\underline{C}H_2$), 66.54 ($\underline{C}$H), 62.60 ($\underline{C}H_2$), 33.81 ($\underline{C}H_2$), 33.66 ($\underline{C}H_2$), 29.35 ($\underline{C}H_2$), 29.03 ($\underline{C}H_2$), 24.30 ($\underline{C}H_2$). SEC M_w: 10440, M_n: 10290, PDI: 1.02.

Example 48

Synthesis of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-[G4]-PGLSA-OH - $Pd(OH)_2/C$ (10% w/w) was added to a solution of [G0]-PGLSA-[G1]-PGLAA-[G2]-PGLSA-[G3]-PGLAA-[G4]-PGLSA-bzld (2.084 g, 0.1478 mmol) in THF (80 mL). The flask for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking

for 10 hours. The catalyst was filtered and washed with THF (75 mL). The filtrate was evaporated to give 1.652 g of a colorless, viscous oil (99.1 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 1.62 (m, 80, -CH_2-$C\underline{H}_2$-$C\underline{H}_2$-CH_2-), 2.37 (m, 80, -$C\underline{H}_2$-CH_2-CH_2-$C\underline{H}_2$-), 2.64 (m, 164, -$C\underline{H}_2$-$C\underline{H}_2$-), 3.52 (m, 12, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-), 3.63-3.71 (broad m, 160, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-), 3.80 (m, 6, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-), 4.06 (m, 14, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-), 4.20 (m, 62, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-), 4.30 (m, 60, -$C\underline{H}_2$-$C\underline{H}$-$C\underline{H}_2$-), 5.25 (m, 30, -CH_2-$C\underline{H}$-CH_2-). ^{13}C NMR (100.6 MHz, CD_3OD): δ 173.40 ($\underline{C}$OOR), 173.06 ($\underline{C}$OOR), 172.58 ($\underline{C}$OOR), 75.82 ($\underline{C}$H), 69.90 ($\underline{C}$H), 69.34 ($\underline{C}$H), 67.64 ($\underline{C}H_2$), 62.45 ($\underline{C}H_2$), 62.15 ($\underline{C}H_2$), 60.46 ($\underline{C}H_2$), 33.25 ($\underline{C}H_2$), 28.87 ($\underline{C}H_2$), 28.67 ($\underline{C}H_2$), 25.27 ($\underline{C}H_2$), 24.12 ($\underline{C}H_2$). MALDI-TOF MS 11299.1 m/z $[M+Na]^+$ (Theory: 11276.39 m/z $[M]^+$). SEC M_w: 9150, M_n: 9000, PDI: 1.02.

Example 49

Synthesis of PEG-([G0]-PGLSA-bzld)$_2$ – This example is shown for PEG of 3400 Mw, but we have also used PEG of 10,000 and 20,000 Mw. PEG, M_n=3400, (10.0 g, 2.94 mmol), which was dried under vacuum at 120 °C for three hours, and [2-(*cis*-1,3-*O*-benzylidene glycerol)-N-succinimidyl] succinate (4.03 g, 10.7 mmol) were dissolved in CH_2Cl_2 (100 mL) and stirred under nitrogen. TEA (2.0 mL, 14 mmol) was added by syringe and stirring was continued for 14 hours. Any remaining activated ester was quenched by the addition of fresh TEA (1.0 mL, 7.2 mmol) and n-propanol (1.0 mL, 11 mmol), which was allowed to stir for another 10 hours. After removing most of the solvent, the product was precipitated in cold ethyl ether (700 mL) and collected to yield 11.1 g of a white solid (97 % yield). ^{1}H NMR obtained. Elemental Analysis C: 55.31 %; H 8.58 % (Theory C: 55.56 %; H 8.66 %). MALDI MS M_w: 4020, M_n: 3940, PDI: 1.02. SEC M_w: 3980, M_n: 3950, PDI: 1.03.

Example 50

Synthesis of PEG-([G0]-PGLSA-OH)$_2$ - Pd/C (10 % w/w) was added to a solution of PEG-([G0]-PGLSA-bzld)$_2$ (5.07 g, 1.29 mmol) in 80 mL of 9:1 ethyl acetate/methanol. The apparatus for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 8 hours. The catalyst was filtered off and washed with ethyl acetate (20 mL). The filtrate was evaporated and the remaining white solid was redissolved in a minimal amount of CH_2Cl_2 (15 mL)and precipitated in cold ethyl ether (600 mL) to give 4.52 g of a white solid (93 % yield). ^{1}H NMR obtained. Elemental Analysis C: 53.49 %; H

8.78 % (Theory C: 53.69 %; H 8.85 %). MALDI MS M_w: 3780, M_n: 3730, PDI: 1.01. SEC M_w: 3860, M_n: 3710, PDI: 1.021.

Example 51

Synthesis of PEG-([G1]-PGLSA-bzld)$_2$ - PEG-([G0]-PGLSA-OH)$_2$ (5.81 g, 1.55 mmol), which was dried under vacuum at 80 °C for three hours, and [2-(*cis*-1,3-*O*-benzylidene glycerol)-N-succinimidyl] succinate (4.35 g, 11.5 mmol) were dissolved in CH_2Cl_2 (70 mL) and stirred under nitrogen. TEA (1.75 mL, 13.0 mmol) was added by syringe and stirring was continued for 14 hours. Any remaining activated ester was quenched by the addition of fresh TEA (1.0 mL, 7.2 mmol) and n-propanol (1.0 mL, 11 mmol), which was allowed to stir for another 10 hours. After removing most of the solvent, the product was precipitated in cold ethyl ether (700 mL) and collected to yield 7.15 g (96 % yield). ^{1}H NMR obtained. MALDI MS M_w: 4520, M_n: 4480, PDI: 1.01. SEC M_w: 4420, M_n: 4240, PDI: 1.04.

Example 52

Synthesis of PEG-([G1]-PGLSA-OH)$_2$ - Pd/C (10 % w/w) was added to a solution of PEG-([G1]-PGLSA-bzld)$_2$ (5.53 g, 1.15 mmol) in 80 mL of 9:1 ethyl acetate/methanol. The apparatus for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 8 hours. The catalyst was filtered off and washed with ethyl acetate (20 mL). The filtrate was evaporated and the remaining white solid was redissolved in a minimal amount of CH_2Cl_2 (15 mL) and precipitated in cold ethyl ether (700 mL) to give 4.71 g of a white solid (92 % yield). ^{1}H NMR obtained. MALDI MS M_w: 4320, M_n: 4280, PDI: 1.01. SEC M_w: 4390, M_n: 4230, PDI: 1.04.

Example 53

Synthesis of PEG-([G1]-PGLSA-MA)$_2$ - PEG-([G1]-PGLSA-OH)$_2$ (1.03 g, 0.232 mmol), which was dried under vacuum at 80 °C for three hours, was dissolved in CH_2Cl_2 (40 mL) and stirred under nitrogen before the addition of methacryloyl chloride (1.93 g, 5.12 mmol). TEA (0.80 mL, 5.74 mmol) was added by syringe and stirring was continued for 14 hours. The mixture was diluted with more CH_2Cl_2 (60 mL) and washed twice with 0.1 N HCl (100 mL). After drying with Na_2SO_4, filtering, and removing most of the solvent, the product was precipitated in cold ethyl ether and collected to yield 1.08 g (94 % yield). ^{1}H NMR obtained. SEC M_w: 4610, M_n: 4420, PDI: 1.04.

Example 54

Synthesis of PEG-([G2]-PGLSA-bzld)$_2$ - PEG-([G1]-PGLSA-OH)$_2$ (0.697 g, 0.150 mmol), which was dried under vacuum at 80 °C for three hours, and [2-(*cis*-1,3-*O*-benzylidene glycerol)-N-succinimidyl] succinate (1.01 g, 2.68 mmol) were dissolved in CH_2Cl_2 (30 mL) and stirred under nitrogen. TEA (0.50 mL, 3.59 mmol) was added by syringe and stirring was continued for 14 hours. Any remaining activated ester was quenched by the addition of fresh TEA (1.0 mL, 7.2 mmol) and n-propanol (1.0 mL, 11 mmol), which was allowed to stir for another 10 hours. After removing most of the solvent, the product was precipitated in cold ethyl ether (400 mL) and collected to yield 0.940 g (93 % yield). ^{1}H NMR obtained.

Example 55

Synthesis of ([G1]-PGLSA-MA)$_2$-PEG - ([G1]-PGLSA-OH)$_2$-PEG (0.500 g, 0.113 mmol) was dissolved in DCM (15 mL) and stirred under nitrogen before methacrylic anhydride (0.56 mL, 3.76 mmol) was added by syringe. DMAP (86.0 mg, 0.704 mmol) was added and stirring was continued for 14 hours. Any remaining anhydride was quenched by the addition of methanol (0.1 mL, 3.95 mmol), which was allowed to stir for another 5 hours. The reaction was diluted with DCM (35 mL) and washed with 0.1 N HCl (50 mL) and brine (50 mL). The organic phase was dried with Na_2SO_4 and filtered before the PEG-based dendrimer was precipitated in cold (-20 °C) ethyl ether (300 mL) and collected to yield 0.519 g of a white solid (93 % yield). ^{1}H NMR ($CDCl_3$): δ 1.90 (m, 19, -C$\underline{H}_3$), 2.61 (m, 21, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.42 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.55-3.65 (broad m, 285, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.77 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.09-4.37 (broad m, 29, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 5.22 (m, 2, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.35 (m, 2, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.57 (m, 6, C$\underline{H}$), 6.07 (m, 6, C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 171.89 ($\underline{C}$OOR), 135.84 ($\underline{C}$H), 126.64 ($\underline{C}$H), 70.75 ($\underline{C}$H$_2$), 69.45 ($\underline{C}$H), 62.61 ($\underline{C}$H$_2$), 28.87 ($\underline{C}$H$_2$), 18.43 ($\underline{C}$H$_3$). FTIR: ν (cm^{-1}) 2873 (aliph. C-H stretch), 1736 (C=O). MALDI MS M_w: 5012, M_n: 4897, PDI: 1.02. SEC M_w: 3910, M_n: 3740, PDI: 1.04. T_m = 40.8.

Example 56

Synthesis of ([G2]-PGLSA-bzld)$_2$-PEG - ([G1]-PGLSA-OH)$_2$-PEG (3.25 g, 0.737 mmol), and 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (12.68 g, 23.37 mmol) were dissolved in DCM (50 mL) and stirred under nitrogen. DMAP (0.588 g, 4.81 mmol) was added and stirring was continued for 14 hours. Any remaining anhydride

was quenched by the addition of n-propanol (2.5 mL, 28 mmol), which was allowed to stir for another 5 hours. The reaction was diluted with DCM (50 mL) and washed with 0.1 N HCl (100 mL), saturated sodium bicarbonate (100 mL 3x), and brine (100 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the PEG-based dendrimer was precipitated in cold (-20 °C) ethyl ether (400 mL) and collected to yield 4.57 g of a white solid (91 % yield). ^{1}H NMR ($CDCl_3$): δ 2.61 (broad m, 40, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.72 (broad m, 16, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.43 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.55-3.65 (broad m, 280, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.77 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.13 (broad m, 28, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.22 (broad m, 28, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.69 (m, 8, -CH_2-C$\underline{H}$-CH_2-), 5.20 (m, 6, -CH_2-C$\underline{H}$-CH_2-), 5.50 (s, 8, C$\underline{H}$), 7.32 (m, 24, arom. C$\underline{H}$), 7.46 (m, 16, arom. C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 172.28 ($\underline{C}$OOR), 171.91 ($\underline{C}$OOR), 171.57 ($\underline{C}$OOR), 138.01 ($\underline{C}$H), 129.26 ($\underline{C}$H), 128.48 ($\underline{C}$H), 126.21 ($\underline{C}$H), 101.33 ($\underline{C}$H), 70.56 ($\underline{C}H_2$), 69.50 ($\underline{C}$H), 69.16 ($\underline{C}H_2$), 66.53 ($\underline{C}$H), 64.08 ($\underline{C}H_2$), 29.49 ($\underline{C}H_2$), 29.21 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 2879(aliph. C-H stretch), 1736 (C=O). MALDI MS M_w: 6642, M_n: 6492, PDI: 1.02. SEC M_w: 4860, M_n: 4680, PDI: 1.04. T_m = 31.4.

Example 57

Synthesis of ([G2]-PGLSA-OH)$_2$-PEG - $Pd(OH)_2$/C (10 % w/w) was added to a solution of ([G2]-PGLSA-bzld)$_2$-PEG (3.26 g, 0.500 mmol) in 25 mL of 2:1 DCM/methanol. The apparatus for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 8 hours. The catalyst was filtered off and washed with DCM (20 mL). The PEG-based dendrimer was isolated after evaporation of solvents to give 2.86 g of a white solid (98 % yield). ^{1}H NMR ($CDCl_3$): δ 2.63 (broad m, 56, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.42 (s, 4, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.50-3.67 (broad m, 285, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.72 (broad m, 27, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.14-4.29 (broad m, 32, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.88 (m, 8, -CH_2-C$\underline{H}$-CH_2-), 5.22 (m, 6, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR ($CDCl_3$): δ 172.56 ($\underline{C}$OOR), 172.32 ($\underline{C}$OOR), 76.01 ($\underline{C}$H), 70.78 ($\underline{C}H_2$), 69.56 ($\underline{C}$H), 69.22 ($\underline{C}H_2$), 64.14 ($\underline{C}H_2$), 63.52 ($\underline{C}H_2$), 62.60 ($\underline{C}H_2$), 61.93 ($\underline{C}H_2$), 29.44 ($\underline{C}H_2$), 29.21 ($\underline{C}H_2$), 28.98 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 3452 (OH), 288. (aliph. C-H stretch), 1735 (C=O). MALDI MS M_w: 5910, M_n: 5788, PDI: 1.02. SEC M_w: 5340, M_n: 5210, PDI: 1.03. T_m = 36.5.

Example 58

Synthesis of ([G2]-PGLSA-MA)$_2$-PEG - ([G2]-PGLSA-OH)$_2$-PEG (0.501 g, 0.0863 mmol) was dissolved in DCM (15 mL) and stirred under nitrogen before methacrylic

anhydride (0.50 mL, 3.36 mmol) was added by syringe. DMAP (72.1 mg, 0.990 mmol) was added and stirring was continued for 14 hours. Any remaining anhydride was quenched by the addition of methanol (0.1 mL, 3.95 mmol), which was allowed to stir for another 5 hours. The reaction was diluted with DCM (35 mL) and washed with 0.1 N HCl (50 mL) and brine (50 mL). The organic phase was dried with Na_2SO_4 and filtered before the PEG-based dendrimer was precipitated in cold (-20 °C) ethyl ether (300 mL) and collected to yield 0.534 g of a white solid (90 % yield). ^{1}H NMR ($CDCl_3$): δ 1.89 (m, 47, -C<u>H</u>$_3$), 2.60 (m, 65, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.56-3.67 (broad m, 387, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.77 (t, 2, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 4.12-4.37 (broad m, 81, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 5.21 (m, 13, -CH$_2$-C<u>H</u>-CH$_2$-), 5.33 (m, 7, -CH$_2$-C<u>H</u>-CH$_2$-), 5.56 (m, 16, C<u>H</u>), 6.06 (m, 16, C<u>H</u>). ^{13}C NMR ($CDCl_3$): δ 171.89 (<u>C</u>OOR), 135.84 (<u>C</u>H), 126.64 (<u>C</u>H), 70.75 (<u>C</u>H$_2$), 69.45 (<u>C</u>H), 62.61 (<u>C</u>H$_2$), 28.87 (<u>C</u>H$_2$), 18.43 (<u>C</u>H$_3$). FTIR: ν (cm^{-1}) 2873 (aliph. C-H stretch), 1736 (C=O). %). MALDI MS M_w: 6956, M_n: 6792, PDI: 1.02. SEC M_w: 4580, M_n: 4390, PDI: 1.04. T_m = 27.0.

Example 59

Synthesis of ([G3]-PGLSA-bzld)$_2$-PEG - ([G2]-PGLSA-OH)$_2$-PEG (2.13 g, 0.367 mmol), and 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (12.71 g, 23.43 mmol) were dissolved in DCM (45 mL) and stirred under nitrogen. DMAP (0.608 g, 4.98 mmol) was added and stirring was continued for 14 hours. Any remaining anhydride was quenched by the addition of n-propanol (2.0 mL, 22 mmol), which was allowed to stir for another 5 hours. The reaction was diluted with DCM (55 mL) and washed with 0.1 N HCl (100 mL), saturated sodium bicarbonate (100 mL 3x), and brine (100 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the PEG-based dendrimer was precipitated in cold (-20 °C) ethyl ether (400 mL) overnight and collected to yield 3.35 g of a white solid (92 % yield). ^{1}H NMR ($CDCl_3$): δ 2.61 (broad m, 84, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 2.74 (broad m, 36, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.43 (t, 2, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.56-3.65 (broad m, 278, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.78 (t, 2, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 4.13 (broad m, 60, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.21 (broad m, 60, -C<u>H</u>$_2$-CH-C<u>H</u>$_2$-), 4.69 (m, 16, -CH$_2$-C<u>H</u>-CH$_2$-), 5.19 (m, 14, -CH$_2$-C<u>H</u>-CH$_2$-), 5.50 (s, 16, C<u>H</u>), 7.32 (m, 46, arom. C<u>H</u>), 7.46 (m, 30, arom. C<u>H</u>). ^{13}C NMR ($CDCl_3$): δ 172.28 (<u>C</u>OOR), 171.91 (<u>C</u>OOR), 138.03 (<u>C</u>H), 129.26 (<u>C</u>H), 128.48 (<u>C</u>H), 126.21 (<u>C</u>H), 101.31 (<u>C</u>H), 70.76 (<u>C</u>H$_2$), 69.49 (<u>C</u>H), 69.16 (<u>C</u>H$_2$), 66.53 (<u>C</u>H), 62.47 (<u>C</u>H$_2$), 29.35 (<u>C</u>H$_2$), 29.02 (<u>C</u>H$_2$), 28.83 (<u>C</u>H$_2$). FTIR: ν (cm^{-1}) 2868 (aliph. C-H stretch), 1735 (C=O). MALDI MS M_w: 10215, M_n: 9985, PDI: 1.02. SEC M_w: 7020, M_n: 6900, PDI: 1.02. T_g = -13.6.

Example 60

Synthesis of ([G3]-PGLSA-OH)$_2$-PEG - Pd(OH)$_2$/C (10 % w/w) was added to a solution of ([G3]-PGLSA-bzld)$_2$-PEG (2.88 g, 0.288 mmol) in 30 mL of 2:1 DCM/methanol. The apparatus for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 8 hours. The catalyst was filtered off and washed with DCM (20 mL). The PEG-based dendrimer was isolated after evaporation of solvents to give 2.86 g of a white solid (98 % yield). ^{1}H NMR ((CD$_3$)$_2$CO):δ 2.64 (broad m, 120, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.49-3.60 (broad m, 286, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.64-3.75 (broad m, 33, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.00-4.12 (broad m, 42, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.13-4.29 (broad m, 68, -CH$_2$-C$\underline{H}$-CH$_2$-), 4.64 (t, 2, -CH$_2$-C$\underline{H}$-CH$_2$-), 4.85 (t, 2, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.26 (m, 14, -CH$_2$-C$\underline{H}$-CH$_2$-). ^{13}C NMR ((CD$_3$)$_2$CO): δ 171.85 ($\underline{C}$OOR), 171.64 ($\underline{C}$OOR), 76.09 ($\underline{C}$H), 73.70 ($\underline{C}$H$_2$), 70.56 ($\underline{C}$H), 69.52 ($\underline{C}$H$_2$), 66.19 ($\underline{C}$H), 63.87 ($\underline{C}$H$_2$), 62.31 ($\underline{C}$H$_2$), 61.65 ($\underline{C}$H$_2$), 60.69 ($\underline{C}$H$_2$). FTIR: ν (cm^{-1}) 3432 (OH), 2925 (aliph. C-H stretch), 1734 (C=O). MALDI MS M_w: 8765, M_n: 8575, PDI: 1.02. SEC M_w: 8090, M_n: 7820, PDI: 1.03. T_g = -38.2.

Example 61

Synthesis of ([G3]-PGLSA-MA)$_2$-PEG - ([G3]-PGLSA-OH)$_2$-PEG (0.223 g, 0.0260 mmol) was dissolved in THF (15 mL) and stirred under nitrogen before methacrylic anhydride (1.10 mL, 7.38 mmol) was added by syringe. DMAP (90.0 mg, 0.737 mmol) was added and stirring was continued for 14 hours. Any remaining anhydride was quenched by the addition of methanol (0.2 mL, 7.89 mmol), which was allowed to stir for another 5 hours. The reaction was diluted with DCM (35 mL) and washed with 0.1 N HCl (50 mL) and brine (50 mL). The organic phase was dried with Na_2SO_4 and filtered before the PEG-based dendrimer was precipitated in cold (-20 °C) ethyl ether (300 mL) and collected to yield 0.248 g of a white solid (89 % yield). ^{1}H NMR (CDCl$_3$): δ 1.90 (m, 76, -C$\underline{H}_3$), 2.62 (m, 111, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.56-3.67 (broad m, 285, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.14-4.38 (broad m, 114, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 5.23 (m, 13, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.35 (m, 10, -CH$_2$-C$\underline{H}$-CH$_2$-), 5.56 (m, 25, C$\underline{H}$), 6.07 (m, 25, C$\underline{H}$). ^{13}C NMR (CDCl$_3$): δ 171.87 ($\underline{C}$OOR), 135.91 ($\underline{C}$H), 126.71 ($\underline{C}$H), 70.76 ($\underline{C}$H$_2$), 69.47 ($\underline{C}$H), 62.62 ($\underline{C}$H$_2$), 28.88 ($\underline{C}$H$_2$), 18.43 ($\underline{C}$H$_3$). FTIR: ν (cm^{-1}) 2874 (aliph. C-H stretch), 1734 (C=O). MALDI MS M_w: 10722, M_n: 10498, PDI: 1.02. SEC M_w: 7000, M_n: 6820, PDI: 1.03. T_g = -37.9.

Example 62

Synthesis of ([G4]-PGLSA-bzld)$_2$-PEG - ([G3]-PGLSA-OH)$_2$-PEG (1.82 g, 0.212 mmol), and 2-(*cis*-1,3-*O*-benzylidene glycerol)succinic acid mono ester anhydride (15.93 g, 29.36 mmol) were dissolved in THF (50 mL) and stirred under nitrogen. DMAP (0.537 g, 4.40 mmol) was added and stirring was continued for 14 hours. Any remaining anhydride was quenched by the addition of n-propanol (2.5 mL, 28 mmol), which was allowed to stir for another 5 hours. The reaction was diluted with DCM (50 mL) and washed with 0.1 N HCl (100 mL), saturated sodium bicarbonate (100 mL 3x), and brine (100 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated before the PEG-based dendrimer was precipitated in ethyl ether (400 mL) and collected to yield 3.11 g of a white solid (87 % yield). ^{1}H NMR ($CDCl_3$): δ 2.61 (broad m, 180, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.70 (broad m, 64, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.43 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.56-3.65 (broad m, 286, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.78 (t, 2, -C$\underline{H}_2$-C$\underline{H}_2$-), 4.11 (broad m, 125, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.23 (broad m, 125, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.68 (m, 32, -CH_2-C$\underline{H}$-CH_2-), 5.20 (m, 30, -CH_2-C$\underline{H}$-CH_2-), 5.49 (s, 32, C$\underline{H}$), 7.32 (m, 93, arom. C$\underline{H}$), 7.46 (m, 62, arom. C$\underline{H}$). ^{13}C NMR ($CDCl_3$): δ 172.28 ($\underline{C}$OOR), 171.90 ($\underline{C}$OOR), 171.60 ($\underline{C}$OOR), 138.04 ($\underline{C}$H), 129.26 ($\underline{C}$H), 128.48 ($\underline{C}$H), 126.21 ($\underline{C}$H), 101.29 ($\underline{C}$H), 70.76 ($\underline{C}H_2$), 69.46 ($\underline{C}$H), 69.15 ($\underline{C}H_2$), 66.53 ($\underline{C}$H), 62.57 ($\underline{C}H_2$), 29.34 ($\underline{C}H_2$), 29.18 ($\underline{C}H_2$), 29.02 ($\underline{C}H_2$), 28.83 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 2865 (aliph. C-H stretch), 1734 (C=O). MALDI MS M_w: 17289, M_n: 16968, PDI: 1.02. SEC M_w: 8110, M_n: 7950, PDI: 1.02. T_g = 5.3.

Example 63

Synthesis of ([G4]-PGLSA-OH)$_2$-PEG - $Pd(OH)_2$/C (10 % w/w) was added to a solution of ([G4]-PGLSA-bzld)$_2$-PEG (2.88 g, 0.170 mmol) in 30 mL of 2:1 DCM/methanol. The apparatus for catalytic hydrogenolysis was evacuated and filled with 60 psi of H_2 before shaking for 8 hours. The catalyst was filtered off and washed with DCM (20 mL). The PEG-based dendrimer was isolated after evaporation of solvents to give 2.86 g of a white solid (98 % yield). ^{1}H NMR ($(CD_3)_2CO$):δ 2.64 (broad m, 248, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.49-3.60 (broad m, 296, -C$\underline{H}_2$-C$\underline{H}_2$-), 3.66 (broad m, 50, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 3.82 (broad m, 42, -C$\underline{H}_2$-CH-C$\underline{H}_2$-), 4.04-4.16 (broad m, 66, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.28 (broad m, 124, -C$\underline{H}_2$-C$\underline{H}$-C$\underline{H}_2$-), 4.86 (m, 10, -CH_2-C$\underline{H}$-CH_2-), 5.27 (m, 30, -CH_2-C$\underline{H}$-CH_2-). ^{13}C NMR ($(CD_3)_2CO$): δ 172.20 ($\underline{C}$OOR), 70.45 ($\underline{C}H_2$), 70.10 ($\underline{C}$H), 69.92 ($\underline{C}H_2$), 65.96 ($\underline{C}$H), 62.31 ($\underline{C}H_2$). FTIR: ν (cm^{-1}) 3445 (OH), 2931 (aliph. C-H stretch), 1713 (C=O). MALDI MS M_w: 14402, M_n: 14146, PDI: 1.02. SEC M_w: 9130, M_n: 8980, PDI: 1.02. T_g = -18.0.

Example 64

Synthesis of bzld-[G1]-PGLSA-TBDPS

4.00 g (0.014 mol) of bzld-[G1]-PGLSA-CO_2H and 3.24 g (0.048 mol) of imidazole were stirred in 15 mL of DMF. Next, 6.4 mL (0.024 mol) of diphenyl-t-butyl silyl chloride were added and the reaction was stirred at 25 °C for 48 hours. The DMF was removed, the product was dissolved in CH_2Cl_2, washed with sat. $NaHCO_3$ and water, dried over Na_2SO_4, filtered, rotovapped, and dried on the vacuum line. The product was purified by column chromatography (4:1 hexanes:EtOAc) affording 6.38 g of product as a viscous opaque oil (86% yield). R_f = 0.13 in 4:1 hexanes:EtOAc. ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 9H, t-butyl), 2.78-2.84 (m, 4H, -CH_2-CH_2), 4.11-4.15 (m, 2H, -CH_2-CH-CH_2-), 4.23-4.26 (m, 2H, -CH_2-CH-CH_2-), 4.70-4.71 (m, 1H, -CH_2-*CH*-CH_2-), 5.54 (s, 1H, *CH*), 7.33-7.42, 7.48-7.50, 7.67-7.68 (m, 15H, arom. bzld and phenyl *CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.34 (-*C*-$(CH_3)_3$), 27.07 (-C-$(CH_3)_3$), 29.72, 30.96 (succ. -CH_2-), 66.46, 69.18 (glycerol, 2C, –CH_2-), 101.39 (O-*C*H-O), 126.23, 127.94, 128.50, 129.28, 130.29, 131.93, 135.51 (arom. *C*H), 137.99 (arom. bzld –*C*-), 171.53, 172.52 (succ. –C(=O)-) ppm. GC-MS: 519.2 m/z (MH^+) (theory: 518.2 m/z (M^+)). HR-FAB: 517.2028 m/z (M-H^+) (theory: 518.2125 m/z (M^+)). Elemental analysis: C, 69.18%; H, 6.69% (theory: C, 69.47%; H, 6.61%).

Example 65

Synthesis of HO-[G1]-PGLSA-TBDPS

2.41 g (4.65 mmol) of bzld-[G1]-PGLSA-TBDPS was dissolved in 45 mL of THF, and 1.0 g of 20% $Pd(OH)_2/C$ was added. The solution was then placed in a Parr tube on a hydrogenator, evacuated, flushed with hydrogen, and shaken under 50 psi H_2 for 3 hours. The solution was then filtered over wet celite. The product was purified by column chromatography (1:1 Hex:EtOAc increasing to 1:4 Hex:EtOAc) to yield 1.9 g of a clear oil (95% yield). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H, t-butyl), 2.02 (b s, 2H, -O*H*), 2.64-2.85 (m, 4H, -CH_2-CH_2), 3.70-3.72, 4.07-4.14 (m, 4H, -CH_2-CH-CH_2-), 4.83-4.86 (m, 1H, -CH_2-*CH*-CH_2-), 7.33-7.44, 7.62-7.65 (m, 10H, arom. phenyl *CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.30 (-*C*-$(CH_3)_3$), 27.03 (-C-$(CH_3)_3$), 29.77, 31.37 (succ. -CH_2-), 62.45 (glycerol, –CH_2-), 75.86 (CH_2-*C*H-CH_2), 127.97, 130.36, 132.67, 135.49 (phenyl *C*H), 172.65, 178.24 (succ. –C(=O)-) ppm. FAB-MS: 431 m/z (M-H^+) (theory: 430.57 m/z (M^+)).

Acetyl derivative of compound HO-[G1]-PGLSA-TBDPS:

Compound HO-[G1]-PGLSA-TBDPS was a hydroscopic oil and repeated attempts to obtain satisfactory EA failed. Thus, we decided to prepare the acetyl analog for elemental analysis. 0.44 g (1.02 mmol) of HO-[G1]-PGLSA-TBDPS was stirred in 30 mL of CH_2Cl_2 with 0.30 g (1.02 mmol) of DPTS, 0.15 mL (2.66 mmol) of freshly distilled acetic acid, and 0.63 g (3.07 mmol) of DCC. The solution was stirred at RT for 18 hours. The DCU precipitate was filtered and the solution was evaporated. A solution of 1:1 ethyl acetate:hexanes was added and impurities precipitated. The solution was filtered, concentrated and further purified by column chromatography (3:1 hexanes:EtOAc), to afford 0.44 g of product (83% yield). $R_f = 0.19$ (4:1 hexanes:EtOAc) ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H, t-butyl), 1.87-1.93 (m, 6H, -C*H*$_3$), 2.50-2.71 (m, 4H, -C*H*$_2$-C*H*$_2$), 3.96-4.19 (m, 4H, -C*H*$_2$-CH-C*H*$_2$-), 5.06-5.18 (m, 1H, -CH$_2$-C*H*-CH$_2$-), 7.22-7.33, 7.51-7.56 (m, 10H, phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.10 (-*C*-(CH$_3$)$_3$), 20.61 (OC-*C*H$_3$), 26.82 (-C-(*C*H$_3$)$_3$), 29.14, 30.62 (succ. -*C*H$_2$-), 62.12, 69.28 (glycerol, –*C*H$_2$-), 127.71, 130.09, 131.65, 135.27 (arom. *C*H), 170.52, 171.19, 171.58 (–*C*(=O)-) ppm. FAB-MS: 515.4 m/z (MH$^+$) (theory: 514.6 m/z (M$^+$)). Elemental analysis: C, 62.76%; H, 6.69% (theory: C, 63.01%; H, 6.66%). SEC: $M_w = 547$, $M_n = 528$, PDI = 1.04.

Example 66

Synthesis of bzld-[G2]-PGLSA-TBDPS

1.90 g (4.41 mmol) of HO-[G1]-PGLSA-TBDPS was stirred in 100 mL of CH_2Cl_2 with 1.30 g (1 equiv; 4.41 mmol) of DPTS, 2.72 g (9.70 mmol; 2.2 equiv) of 2(cis-1,3-*O*-benzylidene glycerol)succinic acid monoester, and 2.00 g (9.70 mmol; 2.2 equiv) of DCC. The solution was stirred at RT for 18 hours. The DCU precipitate was filtered off and the solution was evaporated. A solution of 1:1 ethyl acetate:hexanes was added and impurities precipitated. The solution was filtered, concentrated and further purified by column chromatography (1:1 hexanes:EtOAc) to afford 3.70 g of product (88% yield). $R_f = 0.216$ (1:1 hexanes:EtOAc). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H, t-butyl), 2.57-2.79 (m, 12H, -C*H*$_2$-C*H*$_2$), 4.08-4.14, 4.16-4.22 (m, 12H, -C*H*$_2$-CH-C*H*$_2$-), 4.70-4.71 (m, 2H, -CH$_2$-C*H*-CH$_2$-), 5.21 (m, 1H, C*H*), 5.49-5.54 (m, 1H, C*H*), 7.32-7.41, 7.47-7.49, 7.64-7.58 (m, 20H, arom. bzld and phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.31 (-*C*-(CH$_3$)$_3$), 27.04 (-C-(*C*H$_3$)$_3$), 28.98, 29.33, 30.81 (succ. -*C*H$_2$-), 62.48, 66.50, 69.16, 69.43 (glycerol, –*C*H$_2$-), 101.33 (O-*C*H-O), 126.22, 127.95, 128.49, 129.26, 130.32, 131.92, 135.49 (arom. *C*H), 138.02 (arom. bzld –*C*-), 171.93, 172.28 (succ. –C(=O)-) ppm. GC-MS: 955.3 m/z (MH$^+$) (theory: 954.4

m/z (M^+)). Elemental analysis: C, 64.35%; H, 6.29% (theory: C, 64.14%; H, 6.12%). SEC: $M_w = 940$, $M_n = 930$, PDI = 1.01.

Example 67

Synthesis of bzld-[G2]-PGLSA-acid

1.00 g (1.04 mmol) of of bzld-[G2]-PGLSA-TBDPS was dissolved in 75 mL of THF. Next, 1.25 g (3.96 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution and it was stirred at RT for 1 hour. After one hour the reaction was complete as indicated by TLC. The solution was diluted with 25 mL of H_2O and acidified with 1N HCl to a pH of 3. The product was extracted into CH_2Cl_2, dried over Na_2SO_4, concentrated and dried on the vacuum line. The product was purified by column chromatography (0-5% MeOH in CH_2Cl_2; $R_f = 0.24$) for 0.65 g of product (87% yield). ^{1}H NMR ($CDCl_3$): δ 2.55-2.77 (m, 12H, -CH_2-CH_2), 4.10-4.17, 4.24-4.31 (m, 12H, -CH_2-CH-CH_2-), 4.74-4.75 (m, 2H, -CH_2-*CH*-CH_2-), 5.28-5.31 (m, 1H, *CH*), 5.52-5.54 (m, 2H, *CH*), 7.33-7.38, 7.47-7.49 (m, 10H, arom. bzld *CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 28.72, 29.03, 29.38 (succ. -CH_2-), 62.68, 66.56, 69.16 (glycerol, –CH_2-), 101.44 (O-*C*H-O), 126.23, 128.50, 129.33 (arom. *C*H), 137.75 (arom. bzld –*C*-), 172.67, 175.16 (succ. –C(=O)-) ppm. GC-MS: 715.2 m/z ($M-H^-$) (theory: 716.2 m/z (M^+)). Elemental analysis: C, 58.71%; H, 5.82% (theory: C, 58.66%; H, 5.63%). SEC: $M_w = 810$, $M_n = 800$, PDI = 1.01.

Example 68

Synthesis of HO-[G2]-PGLSA-TBDPS

1.55 g (1.62 mmol) of of bzld-[G2]-PGLSA-TBDPS was dissolved in 40 mL of THF and 1.0 g of 20% $Pd(OH)_2$/C was added. The solution was then placed in a Parr tube on a hydrogenator and shaken under 50 psi H_2 for 4 hours. The solution was then filtered over wet celite, rotoevaporated, and purified by column chromatography (0-25% acetone in EtOAc) to yield 1.12 g of product (95% yield). $R_f = 0.25$ (1:3 acetone:EtOAc). ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, t-butyl), 2.25 (b s, 4H, -O*H*), 2.58-2.82 (m, 12H, -CH_2-CH_2), 3.71-3.74, 4.09-4.26 (m, 12H, -CH_2-CH-CH_2-), 4.87-4.99, 5.24-5.25 (m, 3H, -CH_2-*CH*-CH_2-), 7.34-7.43, 7.63-7.48 (m, 10H, phenyl *CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 14.52 (-*C*-$(CH_3)_3$), 25.78 (-C-$(CH_3)_3$), 26.99, 29.30, 30.51, 30.81 (succ. -CH_2-), 62.08, 63.44, 68.17, 70.23 (glycerol, –CH_2-), 125.71, 127.96, 130.35, 135.45 (phenyl), 171.94, 172.40 (succ. –C(=O)-)

ppm. GC-MS: 779.5 m/z (MH^+) (theory: 778.3 m/z (M^+)). SEC: $M_w = 800$, $M_n = 792$, PDI =1.01

Acetyl derivative of HO-[G2]-PGLSA-TBDPS:

Compound HO-[G2]-PGLSA-TBDPS was a hydroscopic oil and repeated attempts to obtain satisfactory EA failed. Thus, we decided to prepare the acetyl analog for elemental analysis. 0.55 g (0.70 mmol) of of HO-[G2]-PGLSA-TBDPS was stirred in 40 mL of CH_2Cl_2 with 0.39 g (1.34 mmol) of DPTS, 0.19 mL (3.36 mmol) of freshly distilled acetic acid, and 0.87 g (4.20 mmol) of DCC. The solution was stirred at RT for 18 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in a minimum of CH_2Cl_2, cooled to 10 °C and filtered. The resulting solution was concentrated and further purified by column chromatography (0-5% acetone in CH_2Cl_2) to afford 0.49g of product (66% yield). $R_f = 0.17$ (5% acetone in CH_2Cl_2) ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, t-butyl), 2.04 (s, 12H, -C*H*$_3$), 2.55-2.83 (m, 12H, -C*H*$_2$-C*H*$_2$), 4.09-4.32 (m, 12H, -C*H*$_2$-CH-C*H*$_2$-), 5.20-5.29 (m, 3H, -CH$_2$-C*H*-CH$_2$-), 7.32-7.44, 7.61-7.67 (m, 10H, phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.10 (-*C*-(CH$_3$)$_3$), 20.67 (OC-*C*H$_3$), 26.82 (-C-(*C*H$_3$)$_3$), 28.60, 28.80, 29.10, 30.59 (succ. -*C*H$_2$-), 62.11, 62.31, 69.39 (glycerol, –*C*H$_2$-), 127.72, 130.09, 131.67, 135.27 (arom. *C*H), 170.50, 171.33, 171.61 (–*C*(=O)-) ppm. FAB-MS: 947.9 m/z (MH^+) (theory: 947.0 m/z (M^+)). Elemental analysis: C, 57.15%; H, 6.26% (theory: C, 57.07%; H, 6.17%). SEC: $M_w = 1075$, $M_n = 1041$, PDI = 1.03.

Example 69

Synthesis of bzld-[G3]-PGLSA-TBDPS

The bzld-**[G3]-PGLSA-**TBDPS dendron was synthesized by two methods, first by coupling of a bzld-**[G2]-PGLSA**-acid dendron to a HO-**[G1]-PGLSA**-TBDPS dendron convergently, and second by coupling compound to a HO-**[G2]-PGLSA**-TBDPS dendron (7) divergently.

Convergently: 1.05 g (1.47 mmol) of bzld-**[G2]-PGLSA**-acid was stirred in 75mL of CH_2Cl_2, and 0.29 g (0.67 mmol) of HO-**[G1]-PGLSA**-TBDPS, 0.20 g (0.67 mmol) DPTS, and 0.41 g (2.00 mmol) DCC were added. The solution was stirred at RT for 48 hours. The DCU precipitate was filtered off and the solution was evaporated. The product was purified by column chromatography (3:7 hexanes: EtOAc, $R_f = 0.08$) with a yield of 0.99 g (82% yield).

Divergently: 0.55 g (0.71 mmol) of a HO-**[G2]-PGLSA**-TBDPS was stirred in 50 mL of CH_2Cl_2, and 0.42 g (1.41 mmol) of DPTS, 0.871 g (3.11 mmol) of 2(cis-1,3-*O*-Benzylidene Glycerol)Succinic Acid Monoester, and 0.64 g (3.12 mmol) of DCC were added. The solution was stirred under nitrogen at RT for 18 hours. The DCU precipitate was filtered and the solution was evaporated. The product was purified by column chromatography (3:7 hexanes:EtOAc) to afford 0.71 g of product (54% yield). R_f = 0.08 (3:7 hexanes:EtOAc). ^{1}H NMR ($CDCl_3$): δ 1.08 (s, 9H, t-butyl), 2.54-2.92 (m, 28H, -CH_2-CH_2), 4.08-4.15, 4.22-4.27 (m, 28H, -CH_2-CH-CH_2-), 4.71 (s, 4H, -CH_2-C*H*-CH_2-), 5.21-5.24 (m, 3H, C*H*), 5.52 (s, 4H, C*H*), 7.31-7.42, 7.42-7.49, 7.65-7.67 (m, 30H, arom. bzld and phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.31 (-*C*-(CH_3)$_3$), 27.04 (-C-(CH_3)$_3$), 29.35, 30.81 (succ. -*C*H_2-), 62.49, 66.53, 69.16, 69.47 (glycerol, –*C*H_2-), 101.33 (O-*C*H-O), 126.21, 127.94, 128.48, 129.26, 130.32, 135.47 (arom. *C*H), 138.02 (arom. bzld –*C*-), 171.90, 172.28 (succ. –C(=O)-) ppm. GC-MS: 1825.6 m/z (M-H$^+$) (theory: 1827.9 m/z (M$^+$)). HR-FAB: 1825.6124 m/z (M-H$^+$) (theory: 1826.6233 m/z (M$^+$)). Elemental analysis: C, 60.66%; H, 5.85% (theory: C, 61.11%; H, 5.85%). SEC: M_w = 1830, M_n = 1810, PDI = 1.01.

Example 70

Synthesis of bzld-[G3]-PGLSA-acid

2.00 g (1.09 mmol) of bzld-[G3]-PGLSA-TBDPS was dissolved in 125 mL of THF. Next, 1.3 g (4.1 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution. The mixture was stirred at RT for 1 hour. After one hour the reaction was complete as indicated by TLC. The solution was diluted with 25 mL of H_2O and acidified with 1N HCl to a pH of 3. The product was extracted into CH_2Cl_2, dried over Na_2SO_4, rotoevaporated and dried on the vacuum line. The product was purified by column chromatography (0-5% MeOH in CH_2Cl_2) to afford 1.44 g of product (83% yield). R_f = 0.21 (5% MeOH in CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 2.58-2.75 (m, 28H, -CH_2-CH_2), 4.11-4.16, 4.19-4.27 (m, 28H, -CH_2-CH-CH_2-), 4.71-4.72 (m, 4H, -CH_2-C*H*-CH_2-), 5.21-5.28 (m, 3H, C*H*), 5.52-5.53 (m, 4H, C*H*), 7.32-7.37, 7.46-7.49 (m, 20H, arom. bzld C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 29.05, 29.36 (succ. -*C*H_2-), 62.51, 66.58, 69.16 (glycerol, –*C*H_2-), 101.36 (O-*C*H-O), 126.21, 128.49, 129.29 (arom. *C*H), 137.95 (arom. bzld –*C*-), 171.83, 173.01 (succ. –C(=O)-) ppm. GC-MS: 1587.5 m/z (M-H$^+$) (theory: 1588.5 m/z (M$^+$)).

Elemental analysis: C, 58.02%; H, 5.60% (theory: C, 58.18%; H, 5.58%). SEC: M_w = 1650, M_n = 1620, PDI = 1.02.

Example 71

Synthesis of HO-[G3]-PGLSA-TBDPS

0.53 g (0.29 mmol) of bzld-[G3]-PGLSA-TBDPS was dissolved in 50 mL of THF in a Parr tube. 0.4 g of 20% $Pd(OH)_2/C$ was added and the flask was evacuated and filled with 50 psi of H_2. The mixture was shaken for 8 hours, then filtered over wet celite. The filtrate was dried to produce a clear oil which was purified by column chromatography (0-50% acetone in EtOAc) to afford 0.38 g of product (88% yield). R_f = 0.23 (1:1 acetone:EtOAc). ^{1}H NMR ($CDCl_3$): δ1.3 (s, 9H, t-butyl), 2.52-2.86 (m, 28H, -C*H*$_2$-C*H*$_2$), 3.44-3.94 (m, 24, -C*H*$_2$-CH-C*H*$_2$- and -O*H*), 4.10-4.38, (m, 12H, -C*H*$_2$-CH-C*H*$_2$-), 4.82-4.92 (m, 4H, C*H*), 5.18-5.30 (m, 3H, C*H*), 7.28-7.43, 7.50-7.54, 7.60-7.66 (m, 10H, phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 19.04 (-*C*-($CH_3)_3$), 24.44 (-C-($CH_3)_3$), 26.76, 27.12, 28.82, 28.97, 29.10, 30.57 (succ. -*C*H$_2$-), 61.17, 62.33, 63.21, 69.30, 75.52 (glycerol, –*C*H$_2$-), 127.72, 130.11, 131.57, 134.36, 135.20 (arom. *C*H), 171.66, 171.72, 171.99, 172.27, 172.38, 172.46 (succ. –C(=O)-) ppm. MALDI-MS: 1475.56 m/z (MH^+) (theory: 1475.5 m/z (M^+)). SEC: M_w = 2101, M_n = 1994, PDI = 1.05.

Acetyl derivative of compound of HO-[G3]-PGLSA-TBDPS:

Compound HO-[G3]-PGLSA-TBDPS was a hydroscopic oil and repeated attempts to obtain satisfactory EA failed. Thus, we decided to prepare the acetyl analog for elemental analysis. 0.24 g (0.16 mmol) of HO-[G3]-PGLSA-TBDPS was stirred in 40 mL of CH_2Cl_2 with 0.19 g (0.65 mmol) of DPTS, 0.09 mL (1.55 mmol) of freshly distilled acetic acid, and 0.40 g (1.94 mmol) of DCC. The solution was stirred at RT for 18 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in a minimum of CH_2Cl_2, cooled to 10 °C and filtered. The resulting solution was concentrated and further purified by column chromatography (8:2 hexanes:EtOAc to 3:7 hexanes:EtOAc) to afford 0.18 g of product (63% yield). R_f = 0.15 (3:7 hexanes:EtOAc) ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, t-butyl), 1.99 (s, 24H, -C*H*$_3$), 2.48-2.78 (m, 28H, -C*H*$_2$-C*H*$_2$), 4.02-4.30 (m, 28H, -C*H*$_2$-CH-C*H*$_2$-), 5.12-5.26 (m, 7H, -CH$_2$-C*H*-CH$_2$-), 7.25-7.38, 7.55-7.61 (m, 10H, phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 18.87 (-*C*-($CH_3)_3$), 20.46 (OC-*C*H$_3$), 26.61 (-C-(*C*H$_3$)$_3$), 26.95, 28.47, 28.55, 28.64, 28.90, 30.39 (succ. -*C*H$_2$-), 61.90, 62.10, 69.02, 69.22 (glycerol, –*C*H$_2$-), 127.52, 129.90, 131.48, 135.05

(arom. *C*H), 170.26, 171.14, 171.40, 171.46 (–*C*(=O)-) ppm. FAB-MS: 1812.2 m/z (MH^+) (theory: 1811.8 m/z (M^+)). Elemental analysis: C, 53.95%; H, 6.12% (theory: C, 53.70%; H, 5.90%). SEC: M_w = 1943, M_n = 1882, PDI = 1.03.

Example 72

Synthesis of bzld-[G4]-PGLSA-TBDPS

The bzld-**[G4]-PGLSA**-TBDPS dendron was synthesized by two methods, first by coupling of bzld-**[G2]-PGLSA**-acid dendron to a HO-**[G2]-PGLSA**-TBDPS dendron convergently, and secondly by coupling the monoester 2(cis-1,3-*O*-Benzylidene Glycerol)Succinic Acid Monoester to a HO-**[G3]-PGLSA**-TBDPS dendron divergently.

Convergently: 0.14 g (0.18 mmol) of HO-**[G2]-PGLSA**-TBDPS was dissolved in 30 mL of CH_2Cl_2. Next, 0.05 g (0.18 mmol) of DPTS, 0.82 g (1.10 mmol) of bzld-**[G2]-PGLSA**-acid and 0.22 g (1.10 mmol) of DCC were added. The solution was stirred at RT under nitrogen for 72 hours. The DCU was filtered, the filtrate was concentrated to dryness and the residue was resuspended in a minimum of cold THF. The solution was filtered, concentrated and purified by column chromatography (1:1 hexanes:EtOAc to 1:4 hexanes:EtOAc, R_f = 0.14) to afford 0.48 g of product (75% yield).

Divergently: 0.38 g (0.26 mmol) of HO-**[G3]-PGLSA**-TBDPS was dissolved in 50 mL of CH_2Cl_2. Next, 1.00 g (3.57 mmol) of 2(cis-1,3-*O*-Benzylidene Glycerol)Succinic Acid Monoester, 0.10 g (0.34 mmol) of DPTS, and 0.656 g (3.57 mmol) of DCC were added to the mixture. The solution was stirred for 48 hours under nitrogen at RT. The DCU precipitate was filtered, concentrated and purified by column chromatography (1:1 hexanes:EtOAc to 1:4 hexanes:EtOAc, R_f = 0.14) to afford 0.572 g of product (60% yield). ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, t-butyl), 2.55-2.77 (m, 60H, -CH_2-CH_2), 4.07-4.15, 4.22-4.25 (m, 60H, -CH_2-CH-CH_2-), 4.70 (s, 8H, -CH$_2$-*CH*-CH$_2$-), 5.19-5.21 (m, 7H, C*H*), 5.51 (s, 8H, C*H*), 7.30-7.40, 7.46-7.48, 7.63-7.65 (m, 50H, arom. bzld and phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 14.40 (-*C*-(CH_3)$_3$), 27.03 (-C-(CH_3)$_3$), 29.02, 29.35 (succ. -CH_2-), 62.47, 66.53, 69.16, 69.49 (glycerol, –CH_2-), 101.31 (O-*C*H-O), 126.21, 127.94, 128.48, 129.26, 135.47 (arom. *C*H), 138.03 (arom. bzld –*C*-), 171.50, 171.90, 172.27 (succ. –C(=O)-) ppm. MALDI-MS: 3574.54 m/z (MH^+) (theory: 3573.54 m/z (M^+)). Elemental analysis: C, 59.49%; H, 5.70% (theory: C, 59.19%; H, 5.74%). SEC: M_w = 3420, M_n = 3350, PDI = 1.02.

Example 73

Synthesis of [G3]-PGLSA-bzld Dendrimer

0.019 g (0.084 mmol) of [G0]-PGLSA-**OH,** 12 was dissolved in 50 mL of CH_2Cl_2. Next, 0.64 g (0.40 mmol) of compound **bzld-**[G3]-PGLSA-**acid**, 0.074 g (0.25 mmol) of DPTS, and 0.10 g of DCC (0.50 mmol) were added. The solution was stirred for 72 hours at RT under nitrogen. The DCU was filtered off and the filtrate was concentrated. The additional DCU was precipitated in cold THF and filtered. The product was purified by column chromatography (0-5% MeOH in CH_2Cl_2) to yield 0.40 g of product (73% yield). ^{1}H NMR ($CDCl_3$): δ 2.60-2.74 (m, 116H, -CH_2-CH_2), 4.08-4.17 (m, 60H, -CH_2-CH-CH_2-), 4.22-4.26 (m, 60H, -CH_2-CH-CH_2-), 4.70 (s, 16H, -CH_2-C*H*-CH_2-), 5.20-5.23 (m, 14H, C*H*), 5.51 (s, 16H, C*H*), 7.32-7.36, 7.46-7.48 (m, 80H, arom. bzld C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 29.02, 29.35 (succ. -*C*H_2-), 62.47, 66.54, 69.16 (glycerol, –*C*H_2-), 101.31 (O-*C*H-O), 126.21, 128.48, 129.26 (arom. *C*H), 138.01 (arom. bzld –*C*-), 171.83, 172.29 (succ. –C(=O)-) ppm. MALDI: 6553.4 m/z (MH^+) (theory: 6552.2 m/z (M^+). Elemental analysis: C, 58.50%; H, 5.48% (theory: C, 58.29%; H, 5.57%). SEC: M_w = 4740, Mn = 4590, PDI = 1.01.

Example 74

Synthesis of [G3]-PGLSA-OH Dendrimer, 14

0.33 g (0.051 mmol) of [G3]-PGLSA-bzld was dissolved in 50 mL of a 9:1 solution of THF and MeOH in a Parr tube. Next, 0.50 g of 20% Pd(OH)2/C was added and the flask was evacuated and filled with 50 psi of H2. The mixture was shaken for 7 hours, then filtered over wet celite. The filtrate was dried to produce 0.25 g of a clear oil (0.049 mmol, 97% yield). ^{1}H NMR (CD_3OD): δ 2.64 (m, 116, -CH2-CH2-), 3.51 (m, 26, -CH2-CH-CH2-), 3.67 (m, 28, -CH2-CH-CH2-), 3.80 (m, 12, -CH2-CH-CH2-), 4.05 (m, 14, -CH2-CH-CH2-), 4.14 (m, 14, -CH2-CH-CH2-), 4.22 (m, 22, -CH2-CH-CH2-), 4.30 (m, 22, -CH2-CH-CH2-), 5.26 (m, 14, -CH2-CH-CH2) ppm. ^{13}C NMR (CD_3OD): δ 28.61 (CH2), 62.41 (CH2), 62.87 (CH2), 65.67 (*C*H_2), 67.64 (*C*H), 69.91 (*C*H), 172.86 (*C*OOR) ppm. MALDI-MS: 5144.8 m/z (MH^+) (theory: 5142.5 m/z (M^+)). Elemental analysis: C, 48.07%; H, 5.84% (theory: C, 48.11%; H, 5.84%). SEC M_w: 5440; M_n: 5370; PDI: 1.01.

Example 75

Synthesis of [G3]-PGLSA-MA Dendrimer (50% derivatized)

0.22 g (0.041 mmol) of [G3]-PGLSA-OH was dissolved in 5 mL of DMF. Next, 0.20 g (1.66 mmol) of DMAP was then added followed by 0.10 mL (0.67 mmol, 0.5 eq. to the peripheral hydroxyl groups on [G3]-PGLSA-OH) of freshly distilled methacrylic anhydride. After 4.5 hours the reaction was complete as indicated by TLC. 0.03 mL (0.67 mmol) of MeOH was added to the reaction and allowed to stir for an additional 20 minutes. The solution was precipitated into 300 mL of cold ethyl ether. The ether was decanted off and the remaining oily reside was diluted with 20 mL of CH_2Cl_2. The organic phase was washed with 1 N HCl and brine. The organic phase was dried over Na_2SO_4, flitered, and concentrated to approximately 2 mL. This concentrated solution was precipitated in 300 mL of cold ethyl ether. The ether was decanted off and the resulting oily residue was dried under reduced pressure to yield 0.20 g of product (78% yield). ^1H NMR ($CDCl_3$): δ 1.90 (s, 42H, -C*H*$_3$), 2.55-2.77 (m, 116H, -C*H*$_2$-C*H*$_2$), 3.61-3.78 (m, 30H, -CH$_2$-C*H*-CH$_2$-), 4.07-4.30 (m, 120H, -C*H*$_2$-CH-C*H*$_2$-), 5.58-5.62 (m, 16H, =C*H*), 6.03-6.16 (m, 16H, =C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 18.24 (-*C*H$_3$), 29.56, 29.75 (succ. –*C*H$_2$-), 61.52, 62.09, 62.14, 65.17, 65.83, 69.39, 69.56, 70.04, 73.23, 75.89 (glycerol –*C*H$_2$-), 171.04, 171.25, 171.37, 171.58, 171.79, 172.14, 172.51 ppm. MALDI-MS: 6224.6 m/z (MH^+) (theory: 6231.6 m/z (M^+)). SEC: M_w = 3525, M_n = 2708, PDI = 1.30.

Example 76

Synthesis of bzld-[G3]-PGLSA-PEG-OMe

0.29 g (0.18 mmol) of **bzld-**[G3]-PGLSA-**acid** was dissolved in 75 mL of CH_2Cl_2. Next 0.45 g (0.09 mmol) of 5000 MW poly(ethylene glycol) mono-methyl ether (PEG-OMe; MALDI-MS: M_w = 5147, M_n = 5074, PDI = 1.01), 0.037 g (0.18 mmol) of DCC, and 0.026 g (0.09 mmol) of DPTS were added to the solution. The solution was stirred under nitrogen at RT for 168 hours. The DCU was filtered and the filtrate was concentrated to dryness. The resulting residue was resuspended in THF, cooled, and the DCU was filtered. The resulting solution was precipitated in ethyl ether. The solid was dissolved in THF, stirred with Amberlyst A-21 ion-exchange resin (Aldrich) (weakly basic resin) to eliminate the excess **9**. The solution was filtered and the filtrate was dried over Na_2SO_4, dissolved in CH_2Cl_2, washed with 0.1 N HCl, and dried over Na_2SO_4 to yield 0.53 g of a solid white product (89% yield). ^1H NMR ($CDCl_3$): δ 2.60-2.73 (m, 28H, -C*H*$_2$-C*H*$_2$), 3.36

(s, MME CH_3) 3.57-3.64 (m, 406H, PEG CH_2), 4.11-4.26 (m, 28H, -CH_2-CH-CH_2-), 4.71 (m, 4H, -CH_2-CH-CH_2-), 5.21-5.23 (m, 3H, *CH*), 5.52-5.54 (m, 4H, *CH*), 7.32-7.37, 7.46-7.49 (m, 20H, arom. bzld C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 29.36, 29.90 (succ. -CH_2-), 62.48, 66.53, 69.17 (glycerol, –CH_2-), 70.77 (PEG, –CH_2-), 101.33 (O-*C*H-O), 126.21, 128.48, 129.26 (arom. *C*H), 137.80 (arom. bzld –*C*-), 171.90 (succ. –C(=O)-) ppm. MALDI-MS: M_w = 6671, M_n = 6628 PDI = 1.01 (theoretical MW = 6588). SEC: M_w = 6990, M_n = 6670, PDI = 1.04.

Example 77

Synthesis of HO-[G3]-PGLSA-PEG-OMe

0.52 g of bzld-[G3]-PGLSA-PEG-OMe was dissolved in 40 mL of THF. Next, 0.10 g of 20% $Pd(OH)_2/C$ was added. The reaction vessel was evacuated and flushed with hydrogen. The solution was shaken for 3 hours under 50 psi H_2 at RT. The $Pd(OH)_2/C$ was removed by filtering over wet celite. The filtrate was dried and precipitated in ethyl ether to yield 0.40 g of an opaque hydroscopic solid (83% yield). ^{1}H NMR ($CDCl_3$): δ 2.60-2.70 (m, 28H, -CH_2-CH_2), 3.36 (s, MME CH_3) 3.53-3.78 (b m, 422H, PEG CH_2 and -CH_2-CH-CH_2-), 4.17-4.27 (m, 12H, -CH_2-CH-CH_2-), 4.92 (m, 4H, -CH_2-CH-CH_2-), 5.21-5.23 (m, 3H, *CH*) ppm. ^{13}C NMR (DMSO): δ 29.14, 29.36 (succ. -CH_2-), 60.25 (-CH_3 OMe), 63.22, 66.54, 69.87 (glycerol, –CH_2-), 70.43 (PEG, –CH_2-), 172.35, 172.57 (succ. –C(=O)-) ppm. MALDI-MS: M_w = 6302, M_n = 6260, PDI = 1.01 (theoretical MW = 6136). SEC: M_w = 6660, M_n = 6460, PDI = 1.03.

Example 78

Synthesis of MA-[G3]-PGLSA-PEG-OMe

0.39 g (0.064 mmol) of HO-[G3]-PGLSA-PEG-OMe was dissolved in 30 mL of CH_2Cl_2. Next, 10 mg (0.08 mmol) of DMAP and 0.15 mL methacrylic anhydride (1.0 mmol) were added and the solution was stirred at RT under nitrogen overnight. The solution was then washed with 0.1 N HCl, dried over Na_2SO_4, condensed, and precipitated in ether to afford 0.41 g of product (96% yield). ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 24 H, -CH_3-methacrylate), 2.63 (m, 28H, -CH_2-CH_2), 3.36 (s, MME CH_3) 3.59-3.67 (m, 406H, PEG CH_2), 4.19-4.39 (m, 28H, -CH_2-CH-CH_2-), 5.24 (m, 4H, -CH_2-CH-CH_2), 5.35 (m, 3H, *CH*), 5.59 (s, 8H, -CH_2- methacrylate), 6.10 (s, 8H, -CH_2- methacrylate) ppm. MALDI-MS: M_w

= 7080, M_n = 7008, PDI = 1.01 (theoretical MW = 6780). SEC: M_w = 6918, M_n = 6465, PDI = 1.07.

Example 79

Synthesis of Myr-[G2]-PGLSA-TBDPS

0.45 g (0.58 mmol) of compound **OH-[G2]-PGLSA-TBDPS** was dissolved in 75 mL of CH_2Cl_2 with 0.63 g (2.77 mmol) of myristic acid(Myr), 0.34 g (1.16 mmol) of DPTS, and 0.72 g (3.47 mmol) of DCC. The reaction was stirred at RT for 16 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in 50 mL of ethanol, cooled to 0 °C for 6 hours and filtered. The precipitate was resuspended in 75 mL of CH_2Cl_2, washed with 75 mL of H_2O, dried over Na_2SO_4, and the solvent evaporated to yield 0.84 g of product (89% yield). ^1H NMR ($CDCl_3$): δ 0.80-0.89 (t, 12H, -CH_3), 1.08 (s, 9H, t-butyl), 1.14-1.34 (m, 80H, myristic -CH_2-), 1.50-1.64 (m, 8H, C(=O)-CH_2-CH_2-CH_2-), 2.22-2.33 (t, 8H, C(=O)-CH_2-CH_2-), 2.53-2.83 (m, 12H, succinic -CH_2-CH_2), 4.08-4.34 (m, 12H, -CH_2-CH-CH_2-), 5.18-5.30 (m, 3H, -CH_2-*CH*-CH_2-), 7.32-7.44, 7.61-7.67 (m, 10H, phenyl *CH*) ppm. ^{13}C NMR ($CDCl_3$): δ 14.25, 22.67, 24.81, 26.85, 28.81, 28.79, 29.12, 29.24, 29.36, 29.53, 29.64, 31.97, 34.05, 61.88, 62.34, 69.17, 127.66, 130.13, 135.28, 138.77, 171.34, 171.69, 173.32 ppm. FAB-MS: 1620.1 m/z (MH^+) (theory: 1620.29 m/z (M^+)). Elemental analysis: C, 68.84%; H, 9.69% (theory: C, 68.94%; H, 9.58%). SEC: M_w = 2168, M_n = 2135, PDI = 1.02.

Example 80

Synthesis of Myr-[G2]-PGLSA-acid

0.81 g (0.50 mmol) of Myr-**[G2]-PGLSA-TBPDS** was dissolved in 100 mL of THF. Next, 0.55 g (1.75 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution. The mixture was stirred at RT for 1 hour. After one hour the reaction was complete as indicated by TLC. The solution was diluted with 25 mL of H_2O and acidified with 1N HCl to a pH of 3. The product was extracted into EtOAc, dried over Na_2SO_4, rotoevaporated and dried on the vacuum line. The product was purified by column chromatography (0-3% MeOH in CH_2Cl_2) to afford 0.60 g of product (87% yield). R_f = 0.23 (3% MeOH in CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 0.82-0.88 (t, 12H, -CH_3), 1.20-1.31 (m, 80H, myristic -CH_2-), 1.53-1.64 (m, 8H, -C(=O)-CH_2-CH_2-CH_2-), 2.26-2.33 (t, 8H, -C(=O)-

CH_2-CH_2-), 2.60-2.68 (m, 12H, -CH_2-CH_2-), 4.11-4.34 (m, 12H, -CH_2-CH-CH_2-), 5.19-5.35 (m, 3H, -CH_2-CH-CH_2-) ppm. ^{13}C NMR ($CDCl_3$): δ 14.16, 22.78, 24.98, 28.56, 28.87, 29.07, 29.24, 29.47, 29.63, 29.87, 32.01, 34.04, 62.02, 62.64, 69.16, 69.93, 171.47, 171.68, 173.51 ppm. FAB-MS: 1382.9 m/z (M-H^+) (theory: 1381.9 m/z (M^+)). Elemental analysis: C, 66.72%; H, 9.91% (theory: C, 66.92%; H, 9.92%). SEC: M_w = 2074, M_n = 2040, PDI = 1.02.

Example 81

Synthesis of 2-benzyl-1,3-di(Myr-[G2]-PGLSA)$_2$-glycerol

0.85 g (0.62 mmol) of compound Myr-**[G2]-PGLSA**-acid was dissolved in 75 mL of CH_2Cl_2 with 0.05 g (0.26 mmol) of 2-benzyl-glycerol, 0.08 g (0.26 mmol) of DPTS, and 0.16 g (0.77 mmol) of DCC. The reaction was stirred at RT for 16 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in 50 mL of ethanol, cooled to 0 °C for 6 hours and filtered. The precipitate was purified by column chromatography (20-50% EtOAc in hexanes) to yield 0.63 g of product (85% yield). R_f = 0.17 (30% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$): δ 0.81-0.88 (t, 24H, -CH_3), 1.17-1.34 (m, 160H, myristic -CH_2-), 1.52-1.63 (m, 16H, C(=O)-CH_2-CH_2-CH_2-), 2.24-2.32 (t, 16H, C(=O)-CH_2-CH_2-), 2.58-2.66 (m, 24H, succinic -CH_2-CH_2), 3.77-3.85 (m, 1H, -CH_2-CH-CH_2-), 4.04-4.38 (m, 28H, -CH_2-CH-CH_2-), 4.59-4.65 (s, 2H, benzyl –CH_2-), 5.17-5.34 (m, 6H, -CH_2-CH-CH_2-), 7.25-7.34 (m, 5H, aromatic CH) ppm. MALDI-MS: 2933.4 m/z (M+Na^+) (theory: 2933.0 m/z (M+Na^+)). Elemental analysis: C, 67.92%; H, 9.79% (theory: C, 67.69%; H, 9.77%). SEC: M_w = 4388, M_n = 4258, PDI = 1.03.

Example 82

Synthesis of 1,3-di(Myr-[G2]-PGLSA)$_2$-glycerol

0.47 g (0.16 mmol) of 2-benzyl-1,3-di(Myr-**[G2]-PGLSA**)$_2$-glycerol was dissolved in 20 mL of THF and 0.5 g of 10% Pd/C was added. The solution was then placed in a Parr tube on a hydrogenator and shaken under 50 psi H_2 for 10 hours. The solution was then filtered over wet celite, rotoevaporated, to yield the product.

Example 83

Synthesis of bz-SA-[G2]-PGLSA-TBDPS

0.77 g (0.99 mmol) of compound **HO-**[G2]-PGLSA-**TBDPS** was dissolved in 75 mL of CH_2Cl_2 with 0.99 g (4.76 mmol) of benzylated succinic acid (bz-sa), 0.58 g (1.98 mmol) of DPTS, and 1.23 g (5.91 mmol) of DCC. The reaction was stirred at RT for 16 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in a minimum of CH_2Cl_2, cooled to 10 °C for 1 hour and filtered. The solution was concentrated under reduced pressure and purified by column chromatorgraphy (30-50% EtOAc in hexanes) to afford 1.21 g of product (79% yield). R_f = 0.18 (40% EtOAc in hexanes). ^1H NMR ($CDCl_3$): δ 1.08 (s, 9H, t-butyl), 2.55-2.81 (m, 28H, succinic -CH_2-CH_2), 4.06-4.37 (m, 12H, -CH_2-CH-CH_2-), 5.11 (s, 8H, benzyl –CH_2-), 5.18-5.29 (m, 3H, -CH_2-CH-CH_2-), 7.22-7.44, 7.61-7.67 (m, 30H, aromatic CH) ppm. ^{13}C NMR ($CDCl_3$): δ 19.13, 26.81, 28.42, 28.64, 28.70, 28.91, 29.07, 30.56, 62.68, 66.72, 69.07, 73.69, 127.68, 128.23, 128.54, 130.06, 131.73, 135.21, 135.77, 171.64, 171.73, 171.90 ppm. FAB-MS: 1539.6 m/z (MH^+) (theory: 1539.7 m/z (M^+)). Elemental analysis: C, 63.35%; H, 6.02% (theory: C, 63.19%; H, 5.89%).

Example 84

Synthesis of bz-SA-[G2]-PGLSA-acid

1.12 g (0.73 mmol) of bz-SA-**[G2]-PGLSA-**TBDPS was dissolved in 100 mL of THF. Next, 0.89 g (2.76 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution. The mixture was stirred at RT for 1 hour. After one hour the reaction was complete as indicated by TLC. The solution was diluted with 25 mL of H_2O and acidified with 1N HCl to a pH of 3. The product was extracted into EtOAc, dried over Na_2SO_4, rotoevaporated and dried on the vacuum line. The product was purified by column chromatography (0-3% MeOH in CH_2Cl_2) to afford 0.71 g of product (75% yield). R_f = 0.18 (3% MeOH in CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.54-2.69 (m, 28H, -CH_2-CH_2), 4.11-4.31 (m, 12H, -CH_2-CH-CH_2-), 5.09 (s, 8H, benzyl –CH_2-), 5.18-5.25 (m, 3H, -CH_2-CH-CH_2-), 7.25-7.36 (m, 20H, aromatic CH) ppm. ^{13}C NMR ($CDCl_3$): δ 28.57, 28.78, 28.94, 62.28, 62.43, 66.60, 69.16, 69.37, 128.24, 128.29, 128.61, 128.57, 171.33, 171.79, 171.95 ppm. FAB-MS: 1301.5 m/z ($M-H^+$) (theory: 1301.3 m/z (M^+)). Elemental analysis: C, 60.23%; H, 5.81% (theory: C, 60.00%; H, 5.58%). SEC: M_w = 1415, M_n = 1379, PDI = 1.03.

Example 85

Synthesis of bz-SA-[G4]-PGLSA-TBDPS

0.07 g (0.08 mmol) of compound **HO-**[G2]-PGLSA-**TBDPS** was dissolved in 40 mL of CH_2Cl_2 with 0.53 g (0.41 mmol) of bz-SA-**[G2]-PGLSA**-acid, 0.05 g (0.17 mmol) of DPTS, and 0.11 g (0.51 mmol) of DCC. The reaction was stirred at RT for 48 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in a minimum of CH_2Cl_2, cooled to 10 °C for 1 hour and filtered. The solution was concentrated under reduced pressure and purified by column chromatorgraphy (30-80% EtOAc in hexanes) to afford 0.40 g of product (80% yield). R_f = 0.18 (65% EtOAc in hexanes). ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 9H, t-butyl), 2.53-2.81 (m, 124H, succinic -CH_2-CH_2), 4.10-4.31 (m, 60H, -CH_2-CH-CH_2-), 5.09 (s, 32H, benzyl -CH_2-), 5.18-5.28 (m, 15H, -CH_2-C*H*-CH_2-), 7.25-7.41, 7.45-7.49, 7.61-7.66 (m, 90H, aromatic C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 26.72, 28.52, 28.73, 28.87, 62.15, 66.43, 68.84, 69.16, 125.91, 127.64, 128.11, 128.33, 128.46, 130.01, 135.16, 135.66, 171.25, 171.54, 171.64, 171.81 ppm. MALDI-MS: XXX m/z (MH^+) (theory: XXX m/z (M^+)). Elemental analysis: C, 60.70%; H, 5.74% (theory: C, 60.34%; H, 5.63%). SEC: M_w = 5142, M_n = 5064, PDI = 1.02.

Example 86

Synthesis of bz-SA-[G4]-PGLSA-acid

0.22 g (0.04 mmol) of bz-SA-**[G4]-PGLSA**-TBDPS was dissolved in 12 mL of THF. Next, 0.04 g (0.13 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution. The mixture was stirred at RT for 4 hours. The solution was diluted with 5 mL of H_2O and acidified with 1N HCl to a pH of 3. Additional THF was added dropwise to keep product in solution. The product was extracted into EtOAc, dried over Na_2SO_4, rotoevaporated and dried on the vacuum line. The product was purified by column chromatography (20-100% EtOAc in hexanes) to afford the product. ^{1}H NMR ($CDCl_3$): δ 2.46-2.84 (m, 124H, -CH_2-CH_2), 4.12-4.49 (m, 60H, -CH_2-CH-CH_2-), 5.02-5.36 (m, 57H, benzyl –CH_2- and -CH_2-C*H*-CH_2-), 7.25-7.48 (m, 80H, aromatic C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ 28.79, 28.93, 62.21, 66.51, 69.24, 127.64, 128.17, 128.52, 135.69, 171.34, 171.73, 171.91 ppm.

Example 87

Synthesis of ZLys(Z)-OPFP

DCC (5.45 g, 26 mmol) was added in five portions over 10 minutes to a solution of ZLys(Z)OH (10 g, 24 mmol) and 1.1 equiv of pentafluorophenol in freshly distilled CH_2Cl_2 (40 ml). The reaction mixture was stirred under N_2 at 25 °C for 2 h, filtered to remove the insoluble urea, concentrated to ~ 20 ml under reduced pressure, and then stored at 4 °C for 2 h. An additional filtration removed further urea, and the filtrate was diluted with hexane (25 ml) and stored at 4 °C for 4h. The resultant white precipitate was collected by filtration, washed with DCM/hexane (1:2, 3x5 ml), and dried in vacuum; yield 13.37 g (98%).^{1}H NMR ($CDCl_3$): δ 1.46 (m, 2, C*H*$_2$-CH$_2$); 1.54 (m, 2, C*H*$_2$-CH$_2$); 1.84 (m, 1, C*H*$_2$-CH); 2.00 (m, 1, C*H*$_2$-CH); 3.19 (m, 2, C*H*$_2$-NH); 4.67 (m, 1, C*H*$_2$-CH); 4.8 (m, 1, N*H*); 5.03 (m, 2, C*H*$_2$-O); 5.11 (s, 2, C*H*$_2$-O); 5.54 (m, 1, N*H*); 7.3 (m, 10, arom C*H*). ^{19}F NMR (CDCl3): δ -162.26 (t, 2, C*F*); -157.60 (t, 1, C*F*); -152.72 (d, 2, C*F*). Elemental analysis: (theory: C, 57.93; H, 4.34) found C, 58.12; H, 4.40

Example 88

Synthesis of ZLys(Z)Lys(ZLys(Z))OMe

LysOMe. 2HCl (1.43 g, 6 mmol) was dissolved in DMF (45 ml) with the DIEA (2.35 g, 18 mmol), and then the HOBT (2.25 g, 14 mmol) was added. After 5 minutes ZLys(Z)OPFP (12.5 g, 21mmol) in DCM (30 ml) was added at 0 °C for 10 minutes. The mixture was stirred for 24 h at RT under N_2. After concentration under vacuum the mixture was dissolved in DCM (50 ml) washed with $NaHCO_3$ (2x150 ml), water (2x150 ml) and then dried over $NaSO_4$. The solvent was removed, and the mixture was precipitated in ether to lead a pure white compound 5.72 g (98%).^{1}H NMR ($CDCl_3$): δ 1.35-1.79 (m, 18, C*H*$_2$-CH$_2$); 2.87 (m, 1, C*H*$_2$-NH); 3.13 (m, 4, C*H*$_2$-NH); 3.40 (m, 1, C*H*$_2$-NH); 3.63 (s, 3, C*H*$_3$); 4.16 (m, 1, C*H*-NH); 4.34 (m, 1, C*H*-NH); 4.38 (m, 1, C*H*-NH); 4.88-5.02 (4 x s, 8, C*H*$_2$-O); 5.13 (m, 1, CH$_2$-N*H*); 5.28 (m, 1, CH$_2$-N*H*); 5.94 (d, 1, CH-N*H*); 6.25 (d, 1, CH-N*H*); 6.88 (m, 1, CH$_2$-N*H*);7.19-7.27 (m, 20, arom C*H*). 7.43 (d, 1, CH-*NH*). FAB MS: 953.4 *m/z* (MH$^+$) (theory: 952.4 *m/z* (M$^+$)). Elemental analysis: (theory: C, 64.27; H, 6.77; N, 8.82; O, 20.14) found C, 63.98; H, 6.79; N, 8.81; O, 20.39.

Example 89

Synthesis of LysLys(Lys)OMe• 4HCl

Pd/C (10% w/w) was added to a solution of ZLys(Z)Lys(ZLys(Z))OMe (1 g, 1mmol) in MeOH (50ml). The flask for catalytic hydrogenolysis was evacuated and filled

with 50 psi of H_2 before shaking for 10 h. The catalyst was filtered and washed with MeOH (20 ml). The filtered was acidified with HCl gas. The acid solution was evaporated to give 578 mg of the white compound (98%).^{1}H NMR (DMSO-d_6): δ 1.36-1.81 (m, 18, CH_2-CH_2); 2.75 (m, 4, CH_2-NH_3^+); 3.12 (m, 2, CH_2-NH); 3.65 (s, 3, CH_3); 3.82 (m, 1, C*H*-NH); 3.98 (m, 1, C*H*-NH); 4.25 (m, 1, C*H*-NH); 8.20-8.45 (m, 12, NH_3^+); 8.88 (t, 1, CH_2-N*H*); 9.18 (d, 1, CH-N*H*). FAB MS: 417.4 *m/z* (MH^+- 4HCl) (theory: 416.3 *m/z* (M^+)). Elemental analysis: (theory: C, 40.65; H, 7.72; Cl, 25.26; N, 14.97) found C, 40.31; H, 7.87; Cl, 25.10; N, 14.97.

Example 90

Synthesis of IsoCysOH

L-cysteine hydrochloride monohydrate (100 g, 0.569 mol) was refluxed in dry acetone (1.5 L) under dry nitrogen for 1.5 hours. The white precipitate was collected by filtration and refluxed a second time in dry acetone. Again the white solid was collected to yield 103.6 g of pure product (92 % yield).

Example 91

Synthesis of IsoCys(Boc)OH

To a suspension of IsoCysOH (144 g, 0.727 mol) and di-*tert*-butyl dicarbonate (206 g, 0.943 mol) in dry acetonitrile was added DIEA (140 mL, 0.803 mol). The suspension was allowed to stir for two days. Afterward, the acetonitrile was removed in vacuo, and the remaining oil was redissolved in ethyl ether and concentrated once more to an oily solid. The oily solid was again dissolved in ethyl ether and the amine salts were removed by vacuum filtration through Celite. The ethereal filtrate was washed with 0.1 N HCl (2x), water (2x), and brine (1x), dried with sodium sulfate, and concentrated to a clear oilt which was dissolved in hexanes and concentrated to a white solid in vacuo. Crystalization from hexanes yielded 142 g of a white solid (75 % yield). FAB MS: 260.1 *m/z* (MH^-) (theory: 261.1 *m/z* (M^+)). Elemental analysis: (theory:50.55; H, 7.33; N, 5.36; O, 24.49; S, 12.27) found C, 50.26; H, 7.30; N, 5.20; S, 12.11.

Example 92

Synthesis of IsoCys(Boc)OPFP

DCC (4.11 g, 20 mmol) was added in five portions over 10 min to a solution of IsoCys(Boc)OH (4.8 g, 18 mmol) and 1.1 equiv of pentafluorophenol (3.42, 20 mmol)in freshly distilled CH_2Cl_2 (25 ml). The reaction mixture was stirred under N_2 at 25 °C for 2 h, filtered to remove the insoluble urea, concentrated to ~ 20 ml under reduced pressure, and then stored at 4 °C for 2 h. An additional filtration removed further urea, and the product was crystallized from hot hexane. The resultant white precipitate was collected by filtration and dried in vacuum; yield 5.8 g (95%).^{1}H NMR ($CDCl_3$): δ 1.43 (s, 6, Boc CH3); 1.49 (s, 3, Boc CH_3); 1.81 (s, 3, Isopr CH_3); 1.87 (s, 3, Isopr CH_3); 3.24 (d-d, 1, CH_2); 3.43 (d-d, 1, CH_2); 5.14 (d, 1, *CH*). ^{19}F NMR (CDCl3): δ -162.24 (t, 2, *CF*); -157.70 (t, 1, *CF*); -152.94 (d, 2, *CF*). GC MS: 445.0 *m/z* (M + NH_4^+) (theory: 427.0 *m/z* (M^+)). Elemental analysis: (theory: C, 47.77; H, 4.25; N, 3.28; S, 7.50) found C, 47.74; H, 4.19; N, 3.35; S, 7.48

Example 93

Synthesis of isoCys(Boc)Lys(isoCys(Boc))Lys(isoCys(Boc)Lys(isoCys(Boc)))OMe

LysLys(Lys)OMe (500 mg, 0.8 mmol) was dissolved in DMF (25 ml) with DIEA (550 mg, 4 mmol, and then HOBT (695 mg, 4 mmol) was added. After 5 minutes the IsoCys(Boc)OPFP, (2.78 g, 5.6 mmol) in DCM (21 ml) was added at 0 °C for 10 minutes. The mixture was stirred for 24 h at RT under N_2. After concentration under vacuum the mixture was dissolved in DCM (40 ml) washed by $NaHCO_3$ (2x100 ml), water (2x100 ml) and dried over $NaSO_4$. Evaporation of organic solvent gave an oil that was purified by silica gel chromatography (DCM-MeOH = 96/4): yield 951 mg (74%).^{1}H NMR ($CDCl_3$): δ 1.19-1.68 (m, 18, CH_2-CH_2); 1.43 (s, 36, Boc CH_3); 1.74 and 1.83 (2 x s, 24, Isopr CH_3); 3.22 (m, 14, CH_2-NH and CH_2-S); 3.68 (s, 3, CH_3-O); 4.29 (m, 1, *CH*-NH); 4.40 (m, 1, *CH*-NH); 4.49 (m, 1, *CH*-NH); 4.69 (m, 4, *CH*-N); 6.40-7.00 (m, 6, *NH*).^{13}C NMR (CDCl3): δ 22.69-25.47 (CH_2); 28.96-30.27 (CH_3); 31.43 (CH_2-S); 34.32; 37.11; 39.98; 52.74-53.32; 67.90; 72.00-74-10 (isopr *C*); 82.05 (Boc *C*); 152.32-154.23 (O-*C*O-NH); 163.17 (*C*O-OCH_3); 171.58-173.07 (*C*O). FAB MS: 1389.6 *m/z* (MH^+) (theory: 1388.6 *m/z* (M^+)). HR MS: 1390.8784 *m/z* (MH^+) (theory: 1390.8799 *m/z* (MH^+)). Elemental analysis: (theory: C, 54.44; H, 7.83; N, 10.08; S, 9.23) found C, 53.93; H, 7.70; N, 9.92; S, 9.15.

Example 94

Synthesis of isoCysLys(isoCys)Lys(isoCysLys(isoCys))OMe•4TFA

TFA (5 ml) was added in 10 portions over 10 min to a solution of isoCys(Boc)Lys(isoCys(Boc))Lys(isoCys(Boc)Lys(isoCys(Boc)))OMe, (600 mg, 0.4 mmol) in freshly distilled CH_2Cl_2 (30 ml) at 0 °C. The reaction mixture was stirred under N_2 for 25 °C for 2 h. The solvent was removed by vacuum, and the mixture was precipitated in ether to afford a pure white compound 417 mg (97 %).^{1}H NMR (CD_3OD): δ 1.39-1.81 (m, 18, C*H*$_2$-CH$_2$); 1.73 (s, 24, Isopr C*H*$_3$); 3.13-3.31 (m, 10, C*H*$_2$-NH); 3.56 (m, 4, C*H*$_2$-S); 3.68 (s, 3, C*H*$_3$-O); 4.27 (m, 1, C*H*-NH); 4.36 (m, 2, C*H*-NH); 4.56 (m, 4, C*H*-NH-C).^{13}C NMR (CD_3OD): δ 24.83-24.96 (*C*H$_2$); 29.43-30.71 (*C*H$_3$); 32.87-33.74 (*C*H$_2$-S); 36.71-36.95 ( ); 40.94-41.38 ( ); 53.68-56.18 ( ); 65.78 ( ); 75.55-75.78 (isopr *C*); 165.31 (*C*O-OCH$_3$); 170.17-174.88 (*C*O). FAB MS: 990.4 *m/z* (MH$^+$) (theory: 989.4 *m/z* (M$^+$)). Elemental analysis: (theory: C, 42.38; H, 5.58; N, 9.69; S, 8.87) found C, 42.10; H, 5.77; N, 9.92; S, 9.01.

Example 95

Synthesis of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl

isoCysLys(isoCys)Lys(isoCysLys(isoCys))OMe,(400 mg, 0.4 mmol) was dissolved in HCl 1N-MeOH 50/50 (60 ml), and stirred under N_2 at 25 °C for 4 h. The solvent was removed by vacuum, and the mixture was precipitated in ether to lead a pure white compound 350 mg (90 %).^{1}H NMR (DMSO d-$_6$): δ 1.30-1.76 (m, 18, C*H*$_2$-CH$_2$); 2.76-3.19 (m, 18, C*H*$_2$-NH, C*H*$_2$-SH and CH$_2$-S*H*); 3.63 (s, 3, C*H*$_3$-O); 4.02 (m, 2, C*H*-NH$_3^+$); 4.13 (m, 2, C*H*-NH$_3^+$); 4.18 (m, 2, C*H*-NH); 4.32 (m, 1, NH-C*H*-CO$_2$CH$_3$); 8.18, 8.47 and 8.81 (m, 18, N*H* and NH$_3^+$). ^{13}C NMR (DMSO d-$_6$): δ 23.34-25.87 (*C*H$_2$); 28.91; 31.99; 49.23; 52.49; 54.56; 167.36 (*C*O-OCH$_3$); 172.26-178.39 (*C*O). FAB MS: 829.6 *m/z* (MH$^+$) (theory: 828.3 *m/z* (M$^+$)). HR MS: 829.3581 *m/z* (MH$^+$) (theory: 828.3478 *m/z* (M$^+$)). Elemental analysis: (theory: C, 38.19; H, 6.62; N, 14.37; S, 13.16) found: C, 37.99; H, 6.67; N, 14.21.

Example 96

Synthesis of the (succinic acid)$_2$-PEG

(OH)$_2$-PEG (10 g, 3 mmol) was dissolved in pyridine (30 ml) with succinic anhydride (5.88 g, 60 mmol), and stirred under N_2 at 25 °C for 4 h. The solvent was

removed by vacuum, and the mixture was precipitated in ether to afford a product 10.48 g (99 %).

Example 97

Synthesis of (succinic acid NHS)$_2$-PEG

(succinic acid)$_2$-PEG (1g, 0.3mmol) was dissolved in DCM with EDCI and DMAP and N-hydroxysuccinimide was added. The reaction was stirred at RT for 24 hours and the product iosolated by precipitation. NMR obtained .

Example 98

Synthesis of (succinic acid cesium salt)$_2$-PEG

(succinic acid)$_2$-PEG (1g, 0.3mmol) was dissolved in water and the pH was adjusted to 7.5 with $CsCO_3$. The solvent was removed to obtain the pure compound (99%).

Example 99

Synthesis of (dimethyl acetal succinic ester)$_2$-PEG

(dimethyl acetal succinic ester)$_2$-PEG was prepared by reaction of (succinic acid cesium salt)$_2$-PEG,(1g, 0.3 mmol), with bromoacetaldehyde dimethyl acetal (133 µl, 1.2mmol) in DMF (5 ml) at 60 °C for 3 days. The solvent was removed by vacuum, and the mixture was precipitated in ether.

Example 100

Synthesis of (dialdehyde succinic ester)$_2$-PEG

(dialdehyde succinic ester)$_2$-PEG was obtain by treatment of (dimethyl acetal succinic ester)$_2$-PEG, with TFA (5% H2O) in CH_2Cl_2 (1:3) at room temperature for 20 minutes. The solvent was removed by vacuum, and the product was precipitated in ethyl ether.

Example 101

Synthesis of PEG-([G1]-PGLSA-NHS)$_2$

PEG-([G1]-PGLSA-OH)$_2$ (1.03 g, 0.232 mmol), which was dried under vacuum at 80 °C for three hours, was then dissolved in CH_2Cl_2 (40 mL). EDCI, DMAP, and N-

hydrosuccinimide were added and the reaction was stirred for 24 hours. The product was isolated by precipitatation in cold ethyl ether.

Example 102

Synthesis of PEG-(lys)$_2$

(NH_2)-PEG (1.0 g), which was dried under vacuum at 80 °C for three hours, was then dissolved in DMF (45 ml) with the DIEA (2.35 g, 18 mmol). HOBT was then added. After 5 minutes ZLys(Z)OPFP in DCM (30 ml) was added at 0 °C for 10 minutes. The mixture was stirred for 24 h at RT under N_2. The reaction was then stopped and the product precipitated in ethyl ether. The Z groups were removed using Pd/C (10% w/w) and hydrogen gas. A solution of the intermediate was dissolved in MeOH (50ml) and pour into the hydrogenation flask. The flask for catalytic hydrogenolysis was evacuated and filled with 50 psi of H_2 before shaking for 10 h. The catalyst was filtered and washed with MeOH (20 ml). The product was isolated by precipitation in ethyl ether..

Example 103

Synthesis of PEG-(lys-succinate-NHS$_2$)$_2$

PEG-(lys)$_2$ (1.0 g), which was dried under vacuum at 80 °C for three hours, was dissolved in CH_2Cl_2 (40 mL) and then succinic anahydride was added. The reaction was stirred for 24 hours and the succinic acid derivatized product was isolated by precipitation in ethyl ether. Next, this intermediate was dissolved in CH_2Cl_2 (40 mL) EDCI, DMAP, and N-hydrosuccinimide were added and the reaction was stirred for 24 hours. The product was isolated by precipitatation in cold ethyl ether.

Example 104

Preparation of a non-covalently crosslinked gel/network using (didodecane methyl amine)$_2$-PEG

The (didodecane methyl amine)$_2$-PEG was prepared in two steps by first treating (NH_2)-PEG with 8 equivalents of bromododecane, 15 equivalents of $NaCO_3$ in reflux ethanol to obtain (didodecane amine)$_2$-PEG. The (didodecane amine)$_2$-PEG, **1**, was then treated with methyl iodine to afford (didodecane methyl amine)$_2$-PEG after precipitation in ether.

This cationic-hydrophobic linear polymer is likely to form a gel with the carboxylated terminated dendritic polymers.

Example 105

General Procedure for the Preparation of an Hydrogel Through Photocrosslinking ([G1]-PGLSA-MA)$_2$-PEG

Five microliters of solution containing 0.5% EY in HEPES buffer (0.1 M, 7.4 pH), 100 μL of 5.0 M TEA, and 1 μL of VP were mixed with 2 mL of a 55 % w/v solution of the dendritic polymer in HEPES buffer. Upon laser exposure (argon ion laser, λ_{max} = 488 and 514 nm, 200 mW) for 60 s, the pink viscous liquid crosslinked into a clear, soft, flexible hydrogel. This reaction can be performed under a variety of concentrations of polymer to prepare gels with different physical and mechanical properties. The crosslinked process can be with a UV or visible light system.

Example 106

General Procedure for the Preparation of an Hydrogel Through Photocrosslinking [G3]-PGLSA-MA

Gels were prepared by dissolving [G3]-PGLSA-MA, DMPA, and VP (1,000:10:1 respectively) in CH_2Cl_2. The polymer solution was exposed to UV light from a UVP BLAK-RAY long wave ultraviolet lamp for 5 minutes. This reaction can be performed under a variety of concentrations of polymer to prepare gels with different physical and mechanical properties. The polymer may be crosslinked with a UV or visible light absorbing system.

Example 107

General Procedure for the Preparation of an Hydrogel Through Photocrosslinking MA-[G3]-PGLSA-PEG-OMe

Five microliters of a solution of 0.5% EY in HEPES buffer (0.1 M, 7.4 pH), 100 μL of 5.0 M TEA, and 1 μL of VP were mixed with 2 mL of a 55 % w/v solution of the dendritic polymer in HEPES buffer. Upon laser exposure (argon ion laser, λ_{max} = 488 and 514 nm, 200 mW) for 60 s, the pink viscous liquid crosslinked into a clear, soft, flexible

hydrogel. This reaction can be performed under a variety of concentrations of polymer to prepare gels with different physical and mechanical properties. The polymer may be crosslinked with a UV or visible light absorbing system.

Example 108

General Procedure for the Preparation of a Hydrogel Through Treatment of LysLys(Lys)OMe with ([G1]-PGLSA-MA)$_2$-PEG

The gel was prepared by mixing an aqueous solution of the LysLys(Lys)OMe dendron with the ([G1]-PGLSA-MA)$_2$-PEG. For example, the dendron dissolved at 33% w/w in phosphate buffer pH=8.2 (10 mg dendron in 20 μl) and the ([G1]-PGLSA-MA)$_2$-PEG was dissolved at 50% w/w (50 mg ([G1]-PGLSA-MA)$_2$-PEG in 50 μL) in the same buffer. These two solutions were mixed together to lead a gel. This reaction can be performed under a variety of concentarations of polymer to prepare gels with much different physical and mechanical properties.

Example 109

General Procedure for the Preparation of a Hydrogel Through Treatment of LysLys(Lys)OMe with PEG n-hydroxysuccinimide ((NHS)$_2$-PEG)

The gel was prepared by mixing an aqueous solution of the LysLys(Lys)OMe dendron with the PEG NHS. For example, the dendron dissolved at 33% w/w in phosphate buffer pH=8.2 (10 mg dendron in 20 μl) and the PEG diNHS (commercially available, Mw = 3400) was dissolved at 55% w/w (50 mg PEG diNHS in 40 μL) in the same buffer. These two solutions were mixed together to lead a gel. Gelation was over in a few minutes. This reaction can be performed under a variety of concentarations of polymer to prepare gels with much different physical and mechanical properties.

Example 110

General Procedure for the Preparation of a Hydrogel Through Treatment of LysLys(Lys)OMe with PEG dimaleimide ((MAL)$_2$-PEG)

The gel was prepared by mixing an aqueous solution of the LysLys(Lys)OMe dendron with the PEG-MAL. For example, the dendron dissolved at 33% w/w in phosphate

buffer pH=8.2 (10 mg dendron in 20 μl) and the PEG dimaleimide (commercially available, Mw = 3400) was dissolved at 55% w/w (50 mg PEG dimaleimide in 40 μL) in the same buffer. These two solutions were mixed together to lead a gel. Gelation occurs over 15 minutes. This reaction can be performed under a variety of concentarations of polymer to prepare gels with much different physical and mechanical properties.

Example 111

General Procedure for the Preparation of a Hydrogel Through Treatment of LysLys(Cys)Lys(CysLys(Cys))OMe•HCl with PEG dialdehdye ($(CHO)_2$-PEG) or (dialdehyde succinic ester)$_2$-PEG

The gel was prepared by mixing an aqueous solution of the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendrons with the peg-dialdehyde or (dialdehyde succinic ester)$_2$-PEG. For example, the dendron dissolved at 33% w/w in phosphate buffer pH=7 (10 mg dendron in 20 μl) and the PEG compound was dissolved at 55% w/w (50 mg PEG in 40 μl) in the same buffer. These two solutions were mixed together to lead a gel. Gelation occurs almost immediately. This reaction can be performed under a variety of concentarations of polymer to prepare gels with much different physical and mechanical properties.

Example 112

General Procedure for the Preparation of a Hydrogel Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with PEG NHS ($(NHS)_2$-PEG)

The gel was prepared by mixing an aqueous solution of the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendrons with the PEG-$(NHS)_2$. For example, the dendron dissolved at 33% w/w in phosphate buffer pH=7 (10 mg dendron in 20 μl) and the PEG compound was dissolved at 55% w/w (50 mg PEG in 40 μl) in the same buffer. These two solutions were mixed together to lead a gel. Gelation occurs almost immediately. This reaction can be performed under a variety of concentarations of polymer to prepare gels with different physical and mechanical properties.

Example 113

General Procedure for the Preparation of a Hydrogel Through the Formation of Disulfide Bonds

The gel was prepared by allowing a solution of 22 mg of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl in 40 μL in phosphate buffered solution to rest for one week. The solution forms a weak hydrogel.

Example 114

General Procedures for the Eye Surgeries Involving a Central Corneal Wound

An enucleated human eye (NC Eye Bank) was placed under a surgical microscope with the cornea facing upwards. The corneal epithelium was scraped with a 4.1 mm keratome blade, and then a 2.75 mm keratome blade was used to incise the central cornea. Next the keratome blade was used to form the 4.1 mm linear or stellate laceration. The wound was closed with either 3 interrupted 10-0 nylon sutures or the photocrosslinkable or self-gelling crosslinkable biodendritic copolymer. Next, a 25 gauge butterfly needle connected to a syringe pump (kdScientific, Model 100 series) was inserted into the scleral wall adjacent to an ocular muscle. In order to measure the wound leaking pressures, the eye was connected to a cardiac transducer via a 20 gauge needle which was inserted 1 cm through the optic nerve. The needle was held in place with surgical tape. The pressure was then recorded. The syringe pump dispensed buffered saline solution (at a rate of 15 - 20 mL/hr) into the eye while the pressure was simultaneously read on the cardiac transducer. The syringe pump rate was maintained to achieve a continuous 1 mm Hg increase in pressure. The leak pressure was recorded as the pressure at which fluid was observed to leak from the eye under the surgical microscope.

Or

The crosslinkable polymer system contained the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG-dialdehyde, PEG-ALD_2 (3400 Mw). The crosslinkable polymer system was then applied to the wound and it sealed the wound in less than 20 seconds. Next, a 25 gauge butterfly needle connected to a syringe pump (kdScientific, Model 100 series) was inserted into the scleral wall adjacent to an ocular muscle. In order to measure the wound leaking pressures, the eye was connected to a cardiac transducer via a 20 gauge needle which was inserted 1 cm through the optic nerve.

The needle was held in place with surgical tape. The pressure was then recorded. The syringe pump dispensed buffered saline solution (at a rate of 15 - 20 mL/hr) into the eye while the pressure was simultaneously read on the cardiac transducer. The syringe pump rate was maintained to achieve a continuous 1 mm Hg increase in pressure. The leak pressure was recorded as the pressure at which fluid was observed to leak from both the nylon suture (N = 6) and biodendrimer sealant (N = 4) treated eyes. For reference, normal intraocular pressure in a human eye is between 15 and 20 mm Hg. The mean leaking pressures (LP) for the sutured treated eyes was 90 mm Hg. The mean leaking pressures (LP) for the polymer treated eyes was approximately the same. Similar results were obtained when using CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG-NHS_2 (3400 Mw PEG), PEG-MAL_2 (3400 Mw PEG), or PEG-dialdehyde to form the hydrogel sealant.

Results using a photocrosslinkable polymer system to seal a central corneal wound

The linear wounds that received sutures had a mean leakage pressure of 78.7 mm Hg with a standard deviation of 27.8 mm Hg. The median leakage pressure was 76.0 mm Hg. The minimum and maximum values were 20 mm Hg and 117 mm Hg, respectively. Examination of the linear wounds that received the adhesive revealed a mean leakage pressure of 109.6 mm Hg with a standard deviation of 82.7 mm Hg. The median leakage pressure was 96.0 mm Hg. The minimum and maximum values were 16 mm Hg and 360 mm Hg, respectively. The calculated p-value for the median leakage pressure between these two groups was 0.390 by the Wilcoxon rank sum test.

The stellate wounds that received sutures had a mean leakage pressure of 57.8 mm Hg with a standard deviation of 28.9 mm Hg. The median leakage pressure was 51.0 mm Hg. The minimum and maximum values were 25 mm Hg and 125 mm Hg, respectively. Analysis of the stellate wounds that received polymer showed a mean leakage pressure of 78.7 mm Hg with a standard deviation of 59.6 mm Hg. The median value was 68.5 mm Hg. The minimum and maximum leakage pressures were 10 mm Hg and 220 mm Hg, respectively. Using the Wilcoxon rank sum test, a p-value of 0.430 was calculated using the median leakage pressure between these two groups.

Example 115

General Procedures for the Eye Surgeries Involving a Clear Corneal Wound

This is the wound made during a cataract procedure. An enucleated human eye was secured under the operating microscope so that the cornea is oriented upwards, facing the microscope. A cardiac transducer(Hewlett-Packard, Palo Alto, CA) was primed and attached a 20-gauge needle (Sherwood Medical, St. Louis, MO) to the end of the saline tubing leading from the transducer. The needle was inserted into the optic nerve approximately 1 cm into the globe. It is not necessary to tie the needle and optic nerve together in order to secure the needle. If the optic nerve has been cut very short, the wound may leak. Eye Bank eyes with little to no optic nerve should not be used. Next, insert a 24-gauge butterfly needle on a saline filled 10-cc syringe (Becton Dickinson & Co., Rutherford, NJ) connected to a syringe pump (KdScientific Model 100) into the anterior chamber through the peripheral cornea. Unless the eyes are very fresh, remove the epithelium by scraping with a blade edge and wipe with Opticel sponges (Wilson Ophthalmic Corp., Mustang, OK). A 3.0 mm dual beveled, angled slit knife (Alcon, Ft. Worth, TX) was used to make a 3.0 mm clear corneal linear incision (perpendicular to the plane of the cornea) 90 degrees from the orientation of the butterfly needle. Place the cardiac monitor on an arterial pressure setting and adjusted to zero mm Hg. Wipe the wound with an Opticel sponge to dry wound. If desired, the edges of the wound can be marked with a pen such as a Devon Skin Marker and Ruler, Regular tip #150 (Tyco Healthcare, Japan). Apply the mixed polymer to the dried wound as advised. Wait for the polymer to cure the advised amount of time. For the suture group, use one interrupted 10-0 nylon suture to close the 3.0 mm clear corneal linear incision using a needle holder and 0.12 forceps. Apply fluoroscein dye using Fluorets strip (Chavvin) to the polymer or wound itself and the surrounding area. Slowly inject saline into the eye via a syringe pump at a rate of 8 mL/hour to slowly increase the IOP as measured by the transducer. Use the cardiac transducer to monitor the IOP of the repaired eyes as done in similar experiments described in the literature. A Tonopen (Medtronic Solan, Jacksonville, FL) can be used to confirm the concordance of the transducer readings at low pressure readings. Check for signs of leakage through the corneal wound or around the polymer sealant. Record the IOP reading from the transducer when leaking through the wound or around the wound (i.e. the leaking pressure) is observed. Qualitatively observe the adherence of the polymer to the enucleated eye following the procedure.

Results using a self-gelling polymer system to seal a clear coneal incision

The clear corneal wound is typically not treated or closed with one 10-0 nylon suture. The clear corneal wounds that received no treatment had a mean leakage pressure of 24 mm Hg with a standard deviation of 8 mm Hg. The median leakage pressure was 21 mm Hg. The clear corneal wounds that received a suture had a mean leakage pressure of 54 mm Hg with a standard deviation of 16 mm Hg. Examination of the linear wounds that received the adhesive, CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG-ALD_2, had a mean leakage pressure of 184 mm Hg with a standard deviation of 79 mm Hg. The median leakage pressure was 181 mm Hg. Similar results were obtained when using CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG-NHS_2, or PEG-MAL_2 (3400 mw PEG) to form the hydrogel sealant.

Example 116

General Procedure for securing a LASIK flap

LASIK (laser-assisted in situ keratomileusis) is the popular refractive surgical procedure where a thin, hinged corneal flap is created by a microkeratome blade. This flap is then moved aside to allow an excimer laser beam to ablate the corneal stromal tissue with extreme precision for the correction of myopia (near-sightedness) and astigmatism. At the conclusion of the procedure, the flap is then repositioned and allowed to heal. However, with trauma, this flap can become dislocated prior to healing, resulting in flap striae (folds) and severe visual loss. When this complication occurs, treatment involves prompt replacement of the flap and flap suturing. The use of sutures has limitations and drawbacks as discussed above. For the LASIK flap study, hinged corneal flaps were created using the Hansatome microkeratome system on four human donor eyebank eyes. Flap adherence was tested with dry Merocel sponges and tying forceps. Biodendrimer tissue adhesive was applied to the entire flap edge and then polymerized with an argon laser beam. The biodendrimer sealant successfully sealed the flap.

OR

Secure enucleated human eye under the operating microscope so that the cornea is oriented upwards, facing the microscope. Apply an 8.5 mm suction ring on the eye and engage

suction. Insert the Hansatome microkeratome handpiece (Bausch and Lomb, St. Louis, MO) with a 180 μm depth plate onto the suction ring and cut a LASIK flap in the cornea. Release the suction and remove the Hansatome microkeratome handpiece and suction ring off the eye. Inspect the quality of the LASIK flap and confirm lack of adherence with a Merocel sponge. Apply the crosslinked hydrogel formulation (CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG-ALD_2, PEG-NHS_2, or PEG-MAL_2 (3400 mw PEG) along the entire flap edge using a metal keratome knife (Alcon, Ft. Worth, TX). Wait for the polymer to cure in the advised amount of time. Retest flap adherence with a Merocel sponge. Inject fluorescein dye from a syringe on a cannula tip underneath the flap through a small incision placed at the flap hinge. Check for leakage of the dye through the flap edge. Qualitatively observe the adherence of the polymer to the enucleated eye following the procedure.

Example 117

Optical Properties of the Dendritic Hydrogel Endocapsular Lens

The gel mixture was prepared directly by mixing together both solutions of dendron CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG dialdehyde. A refractive index measurement was obtained after a 20 min waiting period. The measured refractive index for the gel at 25 ° was 1.41 and at 37 °C was 1.39. The natural lens has a refractive index between 1.399 and 1.425.

Similarily, a gel was prepared by mixing LysLys(Lys)OMe with PEG$(NHS)_2$. Reactive PEGs of Mw of 3400, 10,000, and 20,000 were used. Optimal results were obtained with the large Mw PEG or mixtures of more than one PEG molecular weight. As described above, the dendron and crosslinkable PEG are mixed together in a phosphate buffer at pH 8 or (or pH 9) and a hydrogel forms. Gels were prepared with weight percents ranging from 15 to 50 wt%.

Example 118

Mechanical poperties of the Dendritic Hydrogel Endocapsular Lens

The dendritic macromer (CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG-ALD_2) polymerizes to afford a hydrogel with a high refractive index (monomer and

crosslinking density) while maintaining a desirable, relatively low modulus. This is one feature that distinguishes the use of a dendritic system to create a hydrogel compared to the conventional monomers to form hydrogels from linear polymers. The modulus of the natural lens is $\approx 1 \times 10^3$ Pa (20 year old). Cylindrical hydrogel samples of 8 mm diameter and 2 mm thickness were prepared in buffer and the mechanical properties were measured on a TA instruments 1000 Rheometer at a frequency of 1 Hz. The gels exhibited viscoelastic properties. The complex modulus (G^*) for the 5 to 50 % w/w hydrogels prepared were from $\approx 1 \times 10^2$ to $\approx 1.5 \times 10^4$. These data show that we can prepare hydrogels with similar mechanical properties to the natural lens.

Example 119

General Procedure for the Preparation of an Endocapsular Lens

The crosslinkable formulation is a liquid and thus can be injected using a needle through a small incision. . An enucleated human eye was placed under a surgical microscope with the cornea facing upwards. A clear corneal incision was made and then a small opening in the lens bag was made. Next, the contents of the lens were first removed using a standard phacoemulsification procedure. Once the lens materials was removed, the crosslinkable formulation (CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG-ALD_2 or CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG-NHS_2) was injected into the capsular bag and within several seconds started to form the hydrogel lens. The contents of the bag was filled with the lens dendritic lens material. This procedure on performed on 3 enucleated eyes

Example 120

Method of Encapsulation of a Drug in a Dendritic Polymer

A generation four (G4) poly(glycerol-succinic acid) dendrimer was synthesized in a divergent manner by successive coupling (esterification) and deprotection (hydrogenolysis) reactions with 2-(*cis*-1,3-*O*-benzylidene-glycerol)succinic acid mono ester anhydride and $H_2/Pd(OH)_2$, respectively. A carboxylate terminated G4 dendrimer, (**[G4]-PGLSA**-COONa) was also prepared by reacting the **[G4]-PGLSA**-OH dendrimer with succinic anhydride in pyridine. The hydroxyl (OH) and carboxylated (CO_2H) terminated dendrimers

with molecular weights of 10700 and 18500 amu, respectively, were characterized by NMR, MALDI mass spectrometry, SEC, and quasi-elastic light scattering.

The encapsulation procedure requires both the dendrimer and hydrophobic compound/pharmaceutical to be soluble in a volatile organic solvent that is miscible with water. The following is a typical procedure for the encapsulation of a hydrophobic moiety. First a 1:1 molar ratio of the dendrimer to encapsulant is dissolved in 1.5 - 2.0 mL of methanol, and agitated for 10 minutes. Water (1.0 mL) is then added to the solution and stirred for one hour at ambient temperature. Finally, the methanol is removed over several hours via rotary evaporation.

The encapsulation process can be perfomed with either a third or fourth, but not a first or second generation dendrimer.

__Example 121__

Encapsulation of a 10-Hydroxycamptothecin in a Dendritic Polymer.

10-hydroxycamptothecin (10HCPT) was encapsulated in the dendritic polymer as described above. This poorly water-soluble anticancer drug (≈ 6 μM) was encapsulated in the **[G4]-PGLSA**-COONa dendrimer at a concentration of 200 μM. Initial attempts with the hydroxy terminated **[G4]-PGLSA**-OH dendrimer were less successful. The aromatic and vinyl protons of the encapsulated 10HCPT are clearly visible and distinct from the dendrimer protons in the ^{1}H NMR spectrum (spectrum not shown). The fluorescence spectrum in water of 10HCPT in a **[G4]-PGLSA**-COONa dendrimer shows a λ_{max} at 434 nm (excitation 370 nm).

The encapsulation process can be perfomed with either a third or fourth , but not a first or second generation dendrimer.

__Example 122__

Characterization of a poorly water soluble drug in a dendrimer. Encapsulation of Reichardt's dye in a dendritic polymer.

Characterization data on the dendrimer/encapsulant supramolecular complex is highly desirable. Consequently, we have performed a series of NMR experiments with a model drug "Reichardt's dye" since this poorly water soluble drug (10^{-6} M) possess a large number of aromatic protons. This increases the likelihood for success and allows us to develop the techniques prior to investigating the encapsulated camptothecin. We propose

to a) probe the molecular interactions in the G4 dendrimer/encapsulant complexes using NMR techniques.

We performed a series of 1D and 2D NMR experiments to gain insight into the nature of the encapsulatant-dendrimer complex. Reichardt's dye was selected as the encapsulant model for these experiments since it possesses a large number of aromatic hydrogens. The 1D ^{1}H NMR spectrum in D_2O of the **[G4]-PGLSA-OH** encapsulated dye shows substantial line broading of the aromatic protons compared to unencapsulated Reichardt's dye in CD_3OD. The $\approx$ 5 fold increase in line broadening (FWHM) is attributed to the restricted tumbling of the encapsulated dye. The singlet resonances from the pyridino and phenolato 3,5 protons of the dye in CD_3OD resonate at 8.40 and 6.73 ppm, respectively. When encapsulated in the **[G4]-PGLSA-OH** dendrimer in D_2O, these signals shift downfield to 8.52 and 7.04 ppm, respectively. ^{1}H NMR spin-lattice relaxation time constants (T_1) of these two signals decreased from 1.5 and 1.8 s in CD_3OD to 0.90 and 0.89 s respectively, when encapsulated in the **[G4]-PGLSA-OH** dendrimer in D_2O. Similarly, upon encapsulation, the succinic acid methylenes of the **[G4]-PGLSA-OH** shift upfield from 2.7 to 2.6 ppm as a consequence of the ring current effects associated with the aromatic rings of Reichardt's dye.

Next, ^{1}H 2D NOESY NMR spectra were recorded to explore the molecular interactions between the dendrimer and the encapsulated Reichardt's dye. The NOESY spectra were collected at 25 °C with a mixing time of 450 ms, and NOE between the dye and the dendrimer are clearly observed. The relatively long mixing time was used to provide time for buildup of intermolecular NOEs (which are governed by the specific intermolecular dipole-dipole T_1 relaxation times). The longer mixing times did not change the NOEs. We will conduct experiments with shorter mixing times in the near future. Not only does Reichardt's dye show a number of intramolecular NOE cross peaks among its aromatic protons, but a large number of intermolecular NOE cross peaks are also observed between the aromatic protons of Reichardt's dye and the methylenes of succinic acid and the methines and methylenes of glycerol of the dendrimer demonstrating significant close range NOE dipolar interactions. The extensive network of NOEs raises concerns regarding spin diffusion; however, the differing T_1 relaxation times of the dendrimer and the encapsulant suggest that the cross peaks arise from distinct NOE interactions. Since the intramolecular distance between the pyridino and phenolato 3,5 protons of Reichardt's dye

is about 3 Å, we estimate the intermolecular cross peaks to indicate distances of 5 Å or less between the dye and the dendrimer.

Furthermore, when the 2D NOESY diagonal is phased negative, the off-diagonal NOE cross peaks from the dendrimer and dye also phased negatively. This indicates that all of the NOEs are associated with motions typical of a large macromolecule, further confirming that the dye is encapsulated within the dendrimer. In contrast, when a 2D ^{1}H NMR NOESY spectrum was obtained for the Reichardt's dye in CD_3OD and the diagonal peaks are phased negative, all of the off-diagonal cross peaks are positive, consistent with NOEs of small molecules. These data demonstrate that 1) the dye is tumbling on the same time scale as the dendrimer, and 2) the association between the dye and dendrimer is sufficiently strong to observe significant dipolar through space NOE effects.

Example 123

Cytotoxicity of Encapsulated 10-hydroxycamptothecin in a dendritic polymer.

We evaluated the anticancer activity of the encapsulated 10HCPT using a standard NCI assay. Varying concentrations of **[G4]-PGLSA**-COONa encapsulated 10HCPT were incubated for 0.5 to 2 hours with MCF-7 human breast cancer cells. No cytotoxic effects were observed with the biodendrimer, whereas cell viability was significantly reduced upon incubation with the encapsulated 10HCPT. The highest concentration of encapsulated 10HCPT (20 μM) showed significant activity with less then 10% of the cells remaining viable. These in vitro results demonstrate that the anticancer activity of 10HCPT is retained after encapsulation within the biodendrimer and that the biodendrimer itself is a suitable delivery vehicle for hydrophobic anticancer drugs.

Varying concentrations of **[G4]-PGLSA**-COONa encapsulated 10HCPT were also incubated for 0.5 to 2 hours with colon cancer cells. Similar results were observed with no cytotoxic effects with the biodendrimer, whereas cell viability was significantly reduced upon incubation with the encapsulated 10HCPT.

Example 124

General Procedure for Eye Surgery Involving a Corneal Transplant

An enucleated human eye (NC Eye Bank) or pig eye was placed under a surgical microscope with the cornea facing upwards. A 5.5 mm central corneal trephination was made in an enucleated eye and then this newly formed button will then be autografted

back to the original eye. For the biodendrimer sealant formulations, 20 μL sealant was applied to the wound edges to secure the autograft after 8 or 16 sutures were put into place. Leaking/bursting pressures for all eyes was determined as we have done for the corneal laceration studies. Evidence of major wound leakage or wound dehiscence was used as endpoints for our bursting pressure studies. Fluorescein dye will be applied to the wound and the surrounding area using a Fluorets strip (Chavvin) to look for wound leakage. The use of 8 or 16 sutures affords a wound that leaks at less than 15 mm Hg. Specifically, the crosslinkable polymer sealant system containing the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG(NHS)2, (3400 Mw) was used. The crosslinkable polymer system was applied to the wound and it sealed the wound in less than 20 seconds and the wounds can withstand pressures between 40-60 m Hg. Similar results were obtained using CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG-dialdehyde, PEG-ALD_2, PEG-dialdehyde-ester, or PEG-MAL_2 (3400 Mw PEG) to form the hydrogel sealant. Notably, a graft can also be secured using a photocrosslinked system as described in example 114. For example, 8 or 16 sutures are applied, and then the photocrosslinkable dendritic sealant is applied at the wound interface and crosslinked with an argon ion laser.

Example 125

E-Beam Sterilization of Hydrogel Sealant Formed from CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG(NHS)$_2$

The sealant formulation was sterilized using E-beam. After E-beam sterilization, the dendron and PEG(NHS)$_2$ solutions formed a hydrogel sealant with 30 seconds. Thus, E-beam sterilization is an acceptable sterilization method.

Example 126

Antimicrobial Properties of Hydrogel Formed from CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG(NHS)$_2$ Containing 0.005 wt% Polyhexamethylene biguanide (PHMB)

The antimicrobial properties of a hydrogel containing polyhexamethylene biguanide (PHMB) were tested by incubating the crosslinked adhesive/sealant with the organism Bacillus Atrophaeus (ATCC 9372) at a concentration of 10,000 cfu. The test employed a non-sterile adhesive, a sterile adhesive, and a positive control (N=5/group).

After 24 hours, only the positive control supports the bacteria. Thus, the hydrogel with PHMB adhesive acts as barrier to bacteria.

Example 127

Antimicrobial Properties of Hydrogel Formed from CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG(NHS)$_2$

The antimicrobial properties of the hydrogel were tested by incubating the crosslinked adhesive/sealant with the organism Bacillus Atrophaeus (ATCC 9372) at a concentration of 10,000 cfu. The test employed a non-sterile adhesive, a sterile adhesive, and a positive control (N=5/group). After 24 hours, only the positive control supports the bacteria. Thus, the hydrogel adhesive acts as barrier to bacteria.

Example 128

General Procedure for the Securing a Skin Laceration Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with PEG(NHS)$_2$ to Form a Sealant/Adhesive

A 3 cm by 5 mm incision was made in pigskin through the dermis using a scalpel *ex vivo* (N=3). The wound was dried with a tissue and the crosslinkable polymer sealant system containing the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG(NHS)$_2$, (3400 Mw) was applied as the two edges of the tissue were squeezed. The sealant filled the skin defect and was gelled within 30 seconds.

Example 129

General Procedure for Securing a Liver Laceration Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with PEG(NHS)$_2$ to Form a Sealant/Adhesive

A wound 3 cm long and 5 mm deep was made in chicken liver using a scalpel *ex vivo* (N=3). The wound was dried with a tissue, and the crosslinkable polymer sealant system containing the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl dendron and PEG(NHS)$_2$, (3400 Mw) was applied as the two edges of the tissue were squeezed. The sealant filled the liver injury and was gelled within 30 seconds.

Example 130

Securing a Corneal Incision with a Hydrogel Sealant Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with PEG(NHS)$_2$

The rabbits (N=3) were anesthetized by intramuscular injection of a combination of ketamine hydrochloride and xylazine (34 mg/kg + 5 mg/kg) at a dose of 0.6 mL/kg. Each rabbit was injected subcutaneously with 0.2 mg/kg buprenorphine. Following general anesthesia, a peri-ocular surgical prep was performed by flushing the eyes with a 1:10 dilution of povidone iodine in saline and swabbing the eyelids and surrounding skin. The eyes were flushed with balanced salt solution (BSS), making sure any hair or debris is removed. Following the preparation, an antibiotic-steroid solution, such as Maxitrol® (neomycin/polymyxin/dexamethasone) and 0.5% proparacaine hydrochloride topical anesthetic was instilled into each eye. The rabbit was positioned under the operating microscope and draped. A wire lid speculum was placed. IOP measurement was made prior to the creation of the incision. The conjunctiva was opened and reflected back on the dorsomedial side of the eye. A 2.7-3.0 mm linear incision at the limbus (single plane incision) will be made with a Becton-Dickenson 3 mm slit knife (or equivalent from an alternate manufacturer). At a spot opposite the incision, ~180° limbal, slight pressure (Seidel Test) was applied to the eye with a sterile swab to demonstrate leakage of aqueous humor. Before applying the test material, the incision was dried with a sterile surgical swab. Approximately 0.03 mL of the adhesive was applied and the adhesive was gelled within 30s. Upon application of slight pressure, no leakage was observed and the wound was sealed for all eyes.

Example 131

General Procedure for the Eye Surgeries Involving a Vitrectomy

All extraocular muscle, fat, subconjunctiva and tenon was removed from 16 porcine globes. The globes were cut in half, bisecting the cornea. Uvea, viteous and lens were removed from each hemiglobe and the corneal/scleral shells were individually mounted on a watertight artificial anterior chamber with two-port access. One port was used to infuse balanced salt solution and the other port was attached to a transducer to monitor pressure. Using a 19-guage MVR blade, a pars plana, full-thickness sclerotomy wound was made in each shell perpendicular to the limbus. The wounds were closed using a traditional 3-pass running configuration with 7-0 vicryl suture or with the CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG(NHS) or LysLys(Lys)OMe with PEG

n-hydroxysuccinimide ($(NHS)_2$-PEG). For the hydrogel sealant treatment group, the solution of the adhesive was applied to the wound and the adhesive cured in less than one minute. BSS was then infused into the chamber at a rate of 5mL/hour. Infusion was continued until the wound leaked, at which point the pressure was noted (designated as the leaking pressure). The untreated wounds leaked at an average pressure of 6 mm/Hg mm Hg. The sutured wounds leaked at approximately 140 mm Hg. The wounds treated with the biodendritic adhesive sustained pressures above 225 mm Hg without leaking.

Example 132

General Procedures for the Eye Surgeries Involving a Central Corneal Wound using LysLys(Lys)OMe with PEG n-hydroxysuccinimide ($(NHS)_2$-PEG)

An enucleated human eye (NC Eye Bank) was placed under a surgical microscope with the cornea facing upwards. The corneal epithelium was scraped with a 4.1 mm keratome blade, and then a 2.75 mm keratome blade was used to incise the central cornea. Next the keratome blade was used to form the 4.1 mm linear or stellate laceration. The wound was closed with either 3 interrupted 10-0 nylon sutures or 10-30 mL LysLys(Lys)OMe with PEG n-hydroxysuccinimide ($(NHS)_2$-PEG formulation. Next, a 25 gauge butterfly needle connected to a syringe pump (kdScientific, Model 100 series) was inserted into the scleral wall adjacent to an ocular muscle. In order to measure the wound leaking pressures, the eye was connected to a cardiac transducer via a 20 gauge needle which was inserted 1 cm through the optic nerve. The needle was held in place with surgical tape. The pressure was then recorded. The syringe pump dispensed buffered saline solution into the eye while the pressure was simultaneously read on the cardiac transducer. The syringe pump rate was maintained to achieve a continuous 1 mm Hg increase in pressure. The leak pressure was recorded as the pressure at which fluid was observed to leak from the eye under the surgical microscope. Upon application of the sealant the wound is sealed.

Example 133

General Procedure for the Preparation of a Hydrogel Through Treatment of LysLys(Lys)OMe with tri-block hydrophilic/hydrophobic PEG-PPG-PEG n-hydroxysuccinimide ($(NHS)_2$-PEG-PPG-PEG)

A gel was prepared by mixing an aqueous solution of LysLys(Lys)OMe dendron with PEG-PPG-PEG(NHS)$_2$ (Mn 2900; 40% by wt of PEG). Specifically, the dendron was dissolved in a phosphate buffer at pH=9, and the poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)-diNHS (abreviated as PEG-PPG-PEG(NHS)$_2$) was dissolved in the same buffer but with a pH=8 such that the total weight percent was 15%. These two solutions were mixed together to afford a gel. Gelation was over in a few minutes. This reaction can be performed under a variety of concentrations of polymer to prepare gels with substantially different physical and mechanical properties.

Example 134

General Procedure for the Preparation of a Hydrogel Through Treatment of LysLys(Lys)OMe with tri-block hydrophilic/hydrophobic PEG-PPG-PEG n-hydroxysuccinimide ((NHS)$_2$-PEG-PPG-PEG) and PEG(NHS)$_2$

A gel was prepared by mixing an aqueous solution of LysLys(Lys)OMe dendron with PEG-PPG-PEG(NHS)$_2$ (Mn 2900; 40% by wt of PEG) and PEG(NHS)$_2$ (Mn 3400). Specifically, the dendron was dissolved in a phosphate buffer at pH=9, and PEG-PPG-PEG(NHS)$_2$ and PEG(NHS)$_2$ were dissolved in the same buffer, but with a pH=8 such that the total weight percent was 15%. These two solutions were mixed together to afford a gel. Gelation was over in a few minutes. This reaction can be performed under a variety of concentrations of polymer to prepare gels with substantially different physical and mechanical properties.

Example 135

General Procedure for the Preparation of a Hydrogel Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with tri-block hydrophilic/hydrophobic PEG-PPG-PEG n-hydroxysuccinimide ((NHS)$_2$-PEG-PPG-PEG)

A gel was prepared by mixing an aqueous solution of CysLys(Cys)Lys(CysLys(Cys))OMe dendron with PEG-PPG-PEG(NHS)$_2$ (Mn 2900; 40% by wt of PEG). Specifically, the dendron was dissolved in a phosphate buffer at pH=8.2, and PEG-PPG-PEG(NHS)$_2$ was dissolved in the same buffer such that the total weight percent was 15%. These two solutions were mixed together to afford a gel. Gelation was

over in a few minutes. This reaction can be performed under a variety of concentrations of polymer to prepare gels with substantially different physical and mechanical properties.

Example 136

General Procedure for the Preparation of a Hydrogel Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with tri-block hydrophilic/hydrophobic PEG-PPG-PEG n-hydroxysuccinimide ($(NHS)_2$-PEG-PPG-PEG) and $PEG(NHS)_2$

A gel was prepared by mixing an aqueous solution of CysLys(Cys)Lys(CysLys(Cys))OMe dendron with PEG-PPG-$PEG(NHS)_2$ (Mn 2900; 40% by wt of PEG) and $PEG(NHS)_2$ (Mn 3400). Specifically, the dendron was dissolved in a phosphate buffer at pH=8.2, and PEG-PPG-PEG-$(NHS)_2$ and $PEG(NHS)_2$ were dissolved in the same buffer such that the total weight percent was 15%. These two solutions were mixed together to afford a gel. Gelation was over in a few minutes. This reaction can be performed under a variety of concentrations of polymer to prepare gels with substantially different physical and mechanical properties.

Example 137

General Procedure for the Preparation of a Hydrogel Through Treatment of CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl with the NHS-activated acid of Sebacic Acid (Sebacic Sulfo-n-hydroxysuccinimide ($(NHS\text{-}SO_3)_2$-SA)

A gel was prepared by mixing an aqueous solution of CysLys(Cys)Lys(CysLys(Cys))OMe dendron with Sebacic Sulfo-n-hydroxysuccinimide. Specifically, the dendron was dissolved in a phosphate buffer at pH=8.2 and SA diNHS-SO_3 was dissolved in the same buffer such that the total weight percent was about 30%. These two solutions were mixed together to afford a gel. Gelation was over in a few minutes. This reaction can be performed under a variety of concentrations of polymer to prepare gels with substantially different physical and mechanical properties.

Example 138

General Procedure for the Controlled Polymerization of a Hydrogel Through Combining the Powders CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl and PEG(NHS)$_2$, Co-dissolving the Powders in a Solution Designed to Yield a Final pH Close to pH 6.0, and Passing the Solution Through an Ion Exchange Resin to Rasie the pH to a Level Appropriate for the Two Components to Quickly Crosslink (~pH 7-7.2).

To compare polymerization times, a first gel was prepared by mixing the solids CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl (5.1 mg) and PEG(NHS)$_2$ (36.0 mg, Mn 3400) in a syringe. A solution was prepared containing approximately 100 mM sodium phosphate dibasic and 30 mM sodium carbonate. 230 μl of the solution was drawn into the syringe containing the solids, pushed and pulled between the syringe and the buffer container to mix, and expressed through a cannula. The hydrogel set in approximately 1 minute.

A second gel was prepared by mixing the solids CysLys(Cys)Lys(CysLys(Cys))OMe•4HCl (5.1 mg) and PEG(NHS)$_2$ (36.0 mg, Mn 3400) in a syringe. A solution was prepared of containing approximately 100 mM sodium phosphate dibasic and 30 mM sodium carbonate. 230 μl of the solution was drawn into the syringe containing the solids, pushed and pulled between the syringe and the buffer container to mix, and expressed through a cannula containing a plug of the anion exchange resin MTO-Dowex M43. The hydrogel set in approximately 25 seconds. In this example, the Dowex anion exchange resin serves to remove acid from the initial solution, raising the pH of the overall solution, and, therefore, increasing the rate of polymerization upon expression of the solution.

Incorporation by Reference

All of the patents and publications cited herein are hereby incorporated by reference.

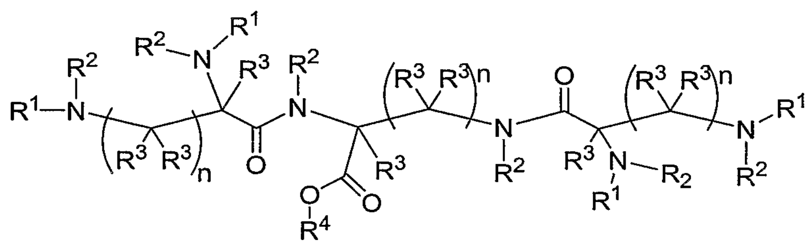
Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

We claim:

1. A method of sealing a wound of a patient, comprising the steps of:

exposing a dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X** to a polymerization agent to form an adhesive composition, and applying said adhesive composition to a wound of a patient, wherein said polymerization agent is an oxidizing agent or a compound of formula **XI**, and wherein formula **VII** is represented by:

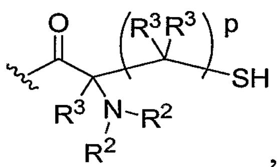
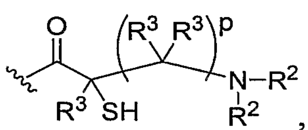
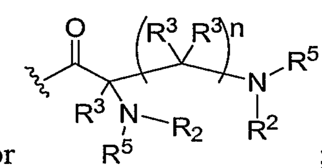


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

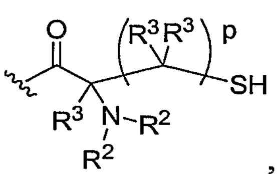
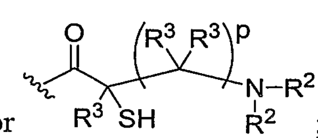
 ,  , or  ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

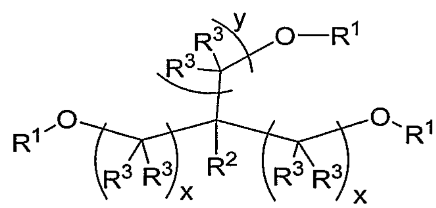
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

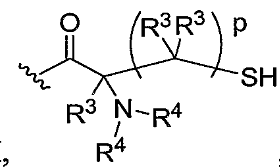
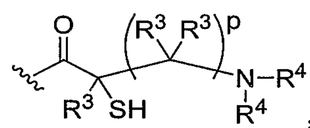
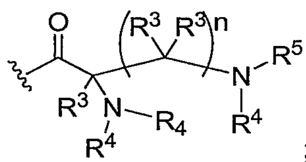
p represents independently for each occurrence 1, 2, 3, 4, or 5;

formula **VIII** is represented by:



VIII

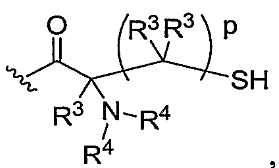
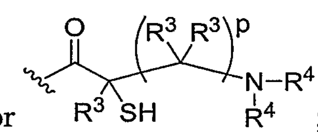
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or  ;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  , or  ;

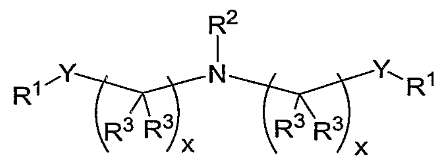
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

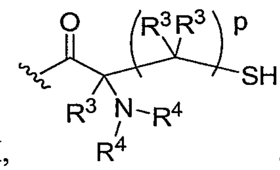
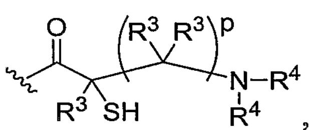
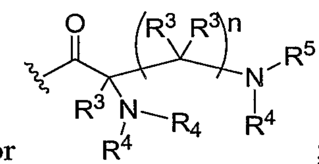
y is 0, 1, 2, 3, or 4;

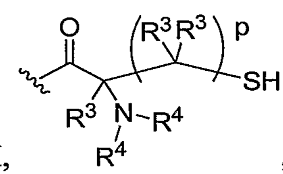
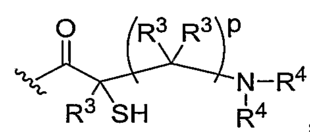
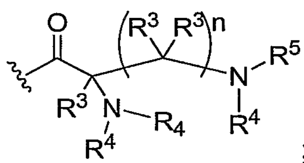
formula **IX** is represented by:



IX

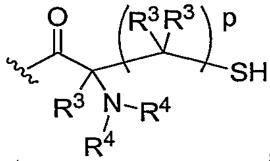
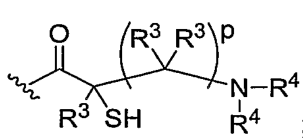
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

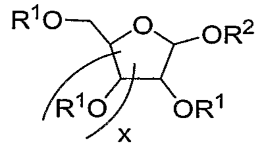
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

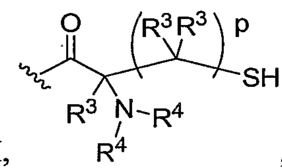
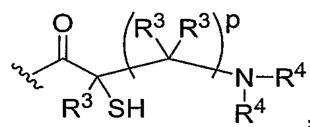
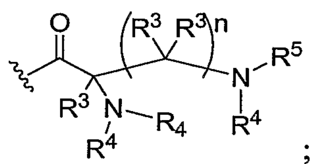
x represents independently for each occurrence 1, 2, 3, or 4;

formula **X** is represented by:



X

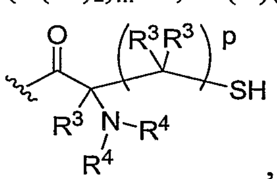
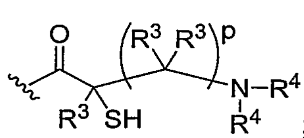
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or  ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  , or  ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2; and

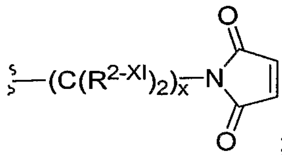
formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

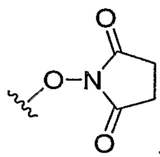
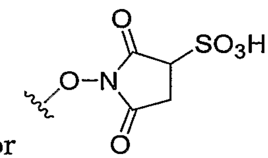
XI

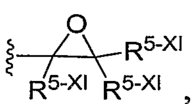
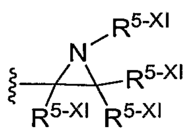
wherein

$R^{1\text{-}XI}$ represents independently for each occurrence $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yR^{4\text{-}XI}$, or

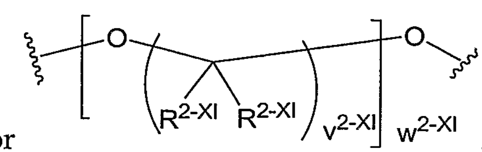

;

$R^{2\text{-}XI}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}XI}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2,  , or  ;

$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S,  , or  ;

$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or  ;

$v^{2\text{-}XI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}XI}$ is an integer in the range of about 5 to 1000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

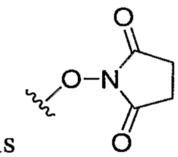
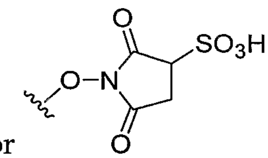
2. The method of claim 1, wherein said polymerization agent is an oxidizing agent.

3. The method of claim 1, wherein said polymerization agent is O_2.

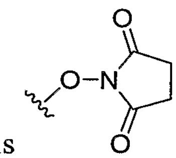
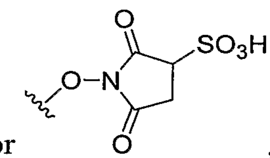
4. The method of claim 1, wherein said polymerization agent is a compound of formula **XI**.

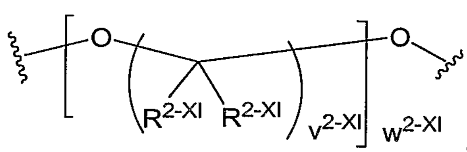
5. The method of claim 4, wherein $w^{2\text{-}XI}$ is an integer in the range of about 50 to about 250.

6. The method of claim 4, wherein $w^{2\text{-}XI}$ is an integer in the range of about 60 to about 90.

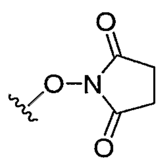
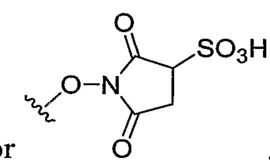
7. The method of claim 4, wherein $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is  or 

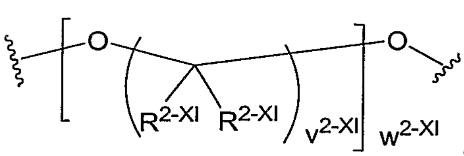
.

8. The method of claim 4, wherein $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or 

, B is 

, and $v^{2\text{-}XI}$ is 2.

9. The method of claim 4, wherein $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or 

, B is 

, $v^{2\text{-}VII}$ is 2, and $w^{2\text{-}XI}$ is an integer in the range of about 15-90.

10. The method of claim 1, wherein said dendrimeric compound is a compound of formula **VII**.

11. The method of claim 10, wherein n is 3, 4, or 5.

12. The method of claim 10, wherein n is 4.

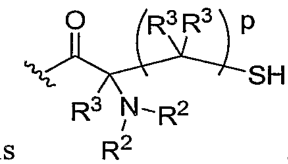
13. The method of claim 10, wherein R^2 is H.

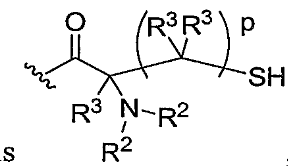
14. The method of claim 10, wherein R^3 is H.

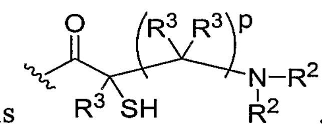
15. The method of claim 10, wherein R^4 is alkyl.

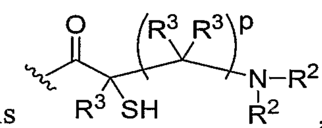
16. The method of claim 10, wherein R^4 is methyl or ethyl.

17. The method of claim 10, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

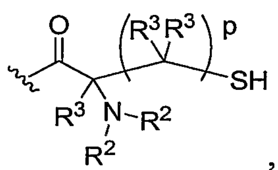
18. The method of claim 10, wherein R^1 is  .

19. The method of claim 10, wherein R^1 is  , and p is 1.

20. The method of claim 10, wherein R^1 is  .

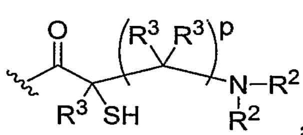
21. The method of claim 10, wherein R^1 is  , and p is 1.

22. The method of claim 10, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is



, and p is 1.

23. The method of claim 10, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is



, and p is 1.

24. The method of claim 1, wherein said dendrimeric compound is a compound of formula **VIII**.

25. The method of claim 1, wherein said dendrimeric compound is a compound of formula **VIII**, x and y are 1, R^2 is $-CH_2OR^1$, and R^3 is H.

26. The method of claim 1, wherein said dendrimeric compound is a compound of formula **VIII**, x is 1, y is 0, and R^2 and R^3 are H.

27. The method of claim 1, wherein said dendrimeric compound is a compound of formula **IX**.

28. The method of claim 1, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is O, R^2 is $-CH_2CH_2OR^1$, and R^3 is H.

29. The method of claim 1, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is NR^4, and R^2 and R^3 are H.

30. The method of claim 1, wherein said dendrimeric compound is a compound of formula **X**.

31. The method of claim 1, wherein said dendrimeric compound is a compound of formula **X**, R^2 is methyl, and x is 2.

32. The method of claim 1, further comprising the step of sterilizing said dendrimeric compound and said polymerization agent.

33. The method of claim 32, wherein said sterilizing is performed by treatment with ethylene oxide, hydrogen peroxide, heat, gamma irradiation, electron beam irradiation, microwave irradiation, or visible light irradiation.

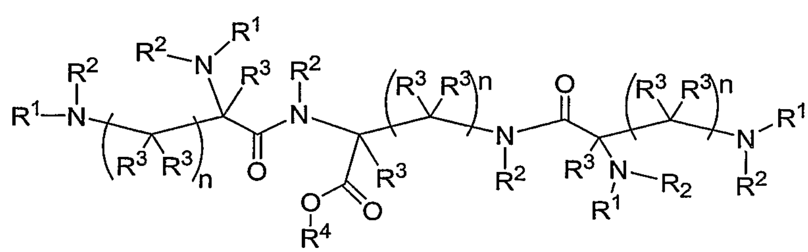
34. The method of any one of claims 1-33, wherein said patient is a primate, bovine, equine, feline, or canine.

35. The method of any one of claims 1-33, wherein said patient is a human.

36. The method of any one of claims 1-35, wherein said wound is an ophthalmic wound.

37. A method of preparing an ocular lens for a patient, comprising the steps of:

exposing a dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X** to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is an oxidizing agent or a compound of formula **XI**, and wherein formula **VII** is represented by:

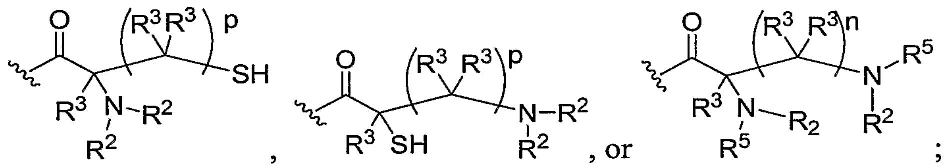


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

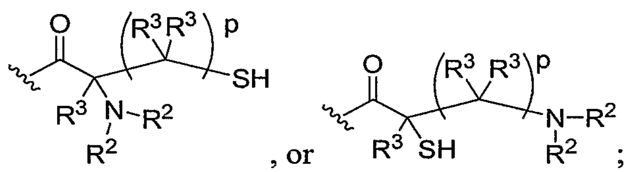


R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

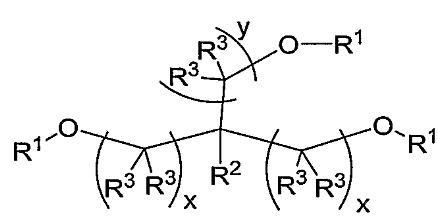
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,



n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

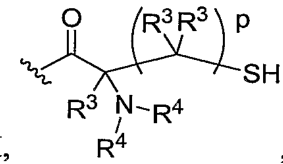
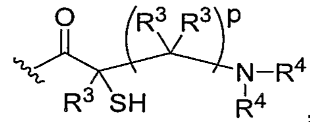
formula **VIII** is represented by:

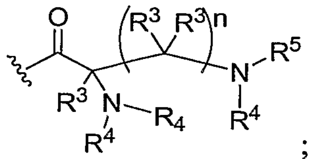


VIII

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$, , , or

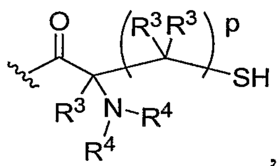
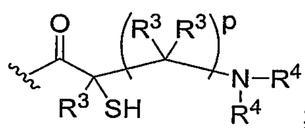
;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

, or ;

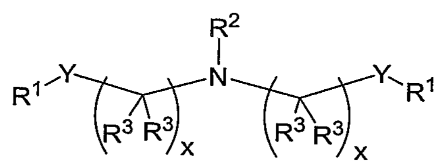
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

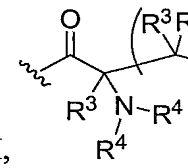
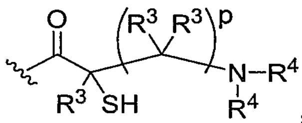
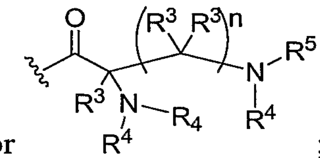
y is 0, 1, 2, 3, or 4;

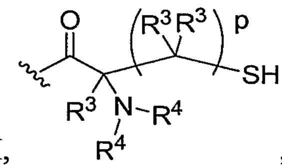
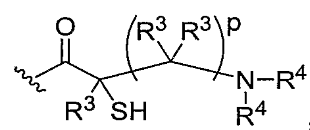
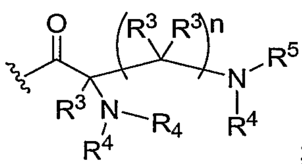
formula **IX** is represented by:



IX

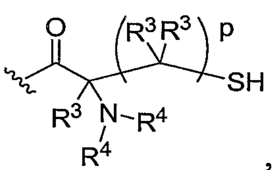
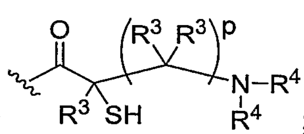
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

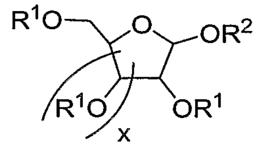
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

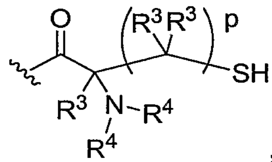
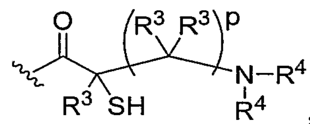
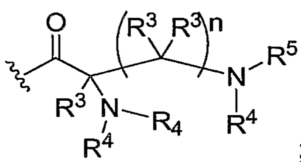
x represents independently for each occurrence 1, 2, 3, or 4;

formula **X** is represented by:



X

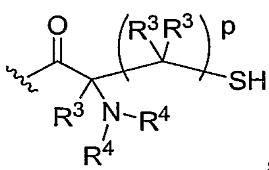
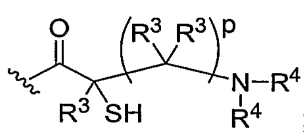
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2; and

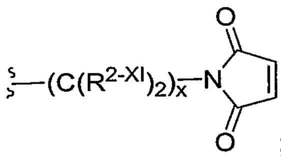
formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

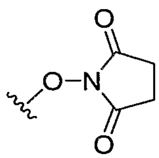
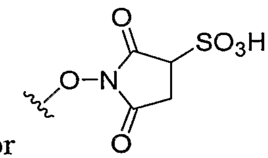
XI

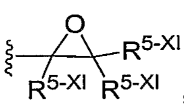
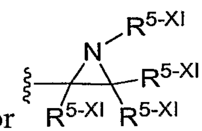
wherein

R^{1-XI} represents independently for each occurrence $-(C(R^{2-XI})_2)_xC(O)R^{3-XI}$, $-C(O)(C(R^{2-XI})_2)_yC(O)R^{3-XI}$, $-(C(R^{2-XI})_2)_xR^{4-XI}$, $-C(O)(C(R^{2-XI})_2)_yR^{4-XI}$, or

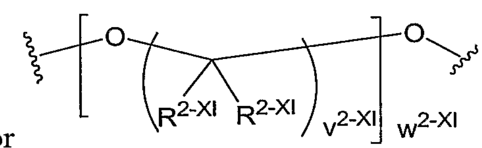

;

R^{2-XI} represents independently for each occurrence H, alkyl, or halogen;

R^{3-XI} represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

R^{4-XI} represents independently for each occurrence -N=C=O, -N=C=S,  , or  ;

R^{5-XI} represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or  ;

v^{2-XI} represents independently for each occurrence 2, 3, or 4;

w^{2-XI} is an integer in the range of about 5 to 7000, inclusive; and

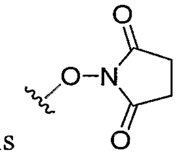
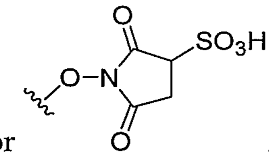
x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

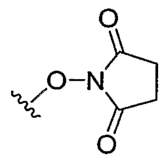
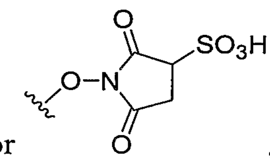
38. The method of claim 37, wherein said polymerization agent is an oxidizing agent.

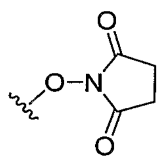
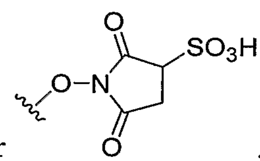
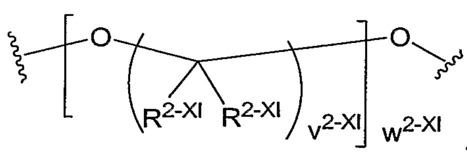
39. The method of claim 37, wherein said polymerization agent is O_2.

40. The method of claim 37, wherein said polymerization agent is a compound of formula **XI**.

41. The method of claim 40, wherein $w^{2\text{-}XI}$ is an integer in the range of about 100 to about 1000.

42. The method of claim 40, wherein $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, and $R^{3\text{-}XI}$ is  or  .

43. The method of claim 40, wherein $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or  , and $v^{2\text{-}XI}$ is 2.

44. The method of claim 40, wherein $R^{1\text{-}XI}$ is $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$ or $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $R^{2\text{-}XI}$ is H, $R^{3\text{-}XI}$ is  or  , B is  , $v^{2\text{-}VII}$ is 2, and $w^{2\text{-}XI}$ is an integer in the range of about 100-1000.

45. The method of claim 37, wherein said dendrimeric compound is a compound of formula **VII**.

46. The method of claim 45, wherein n is 4.

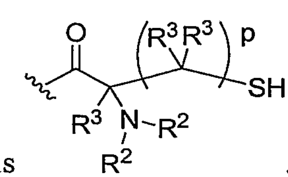
47. The method of claim 45, wherein R^2 is H.

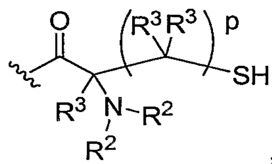
48. The method of claim 45, wherein R^3 is H.

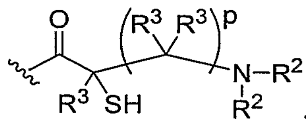
49. The method of claim 45, wherein R^4 is alkyl.

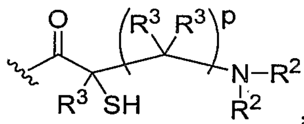
50. The method of claim 45, wherein R^4 is methyl or ethyl.

51. The method of claim 45, wherein n is 4, R^2 and R^3 is H, and R^4 is alkyl.

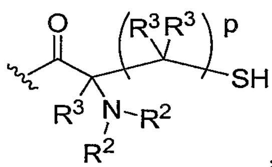
52. The method of claim 45, wherein R^1 is  .

53. The method of claim 45, wherein R^1 is  , and p is 1.

54. The method of claim 45, wherein R^1 is  .

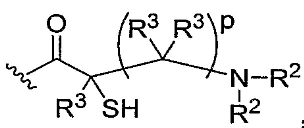
55. The method of claim 45, wherein R^1 is  , and p is 1.

56. The method of claim 45, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is



, and p is 1.

57. The method of claim 45, wherein n is 4, R^2 and R^3 are H, R^4 is methyl, R^1 is



, and p is 1.

58. The method of claim 37, wherein said dendrimeric compound is a compound of formula **VIII**.

59. The method of claim 58, wherein said dendrimeric compound is a compound of formula **VIII**, x and y are 1, R^2 is $-CH_2OR^1$, and R^3 is H.

60. The method of claim 58, wherein said dendrimeric compound is a compound of formula **VIII**, x is 1, y is 0, and R^2 and R^3 are H.

61. The method of claim 58, wherein said dendrimeric compound is a compound of formula **IX**.

62. The method of claim 58, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is O, R^2 is $-CH_2CH_2OR^1$, and R^3 is H.

63. The method of claim 58, wherein said dendrimeric compound is a compound of formula **IX**, x is 2, Y is NR^4, and R^2 and R^3 are H.

64. The method of claim 37, wherein said dendrimeric compound is a compound of formula **X**.

65. The method of claim 64, wherein said dendrimeric compound is a compound of formula **X**, R^2 is methyl, and x is 2.

66. The method of claim 37, further comprising the step of sterilizing said dendrimeric compound, and said polymerization agent, wherein said polymerization agent is a compound of formula **XI**.

67. The method of claim 66, wherein said sterilizing is performed by treatment with ethylene oxide, hydrogen peroxide, heat, gamma irradiation, electron beam irradiation, microwave irradiation, or visible light irradiation.

68. The method of any one of claims 37-67, wherein said patient is a primate, bovine, equine, feline, or canine.

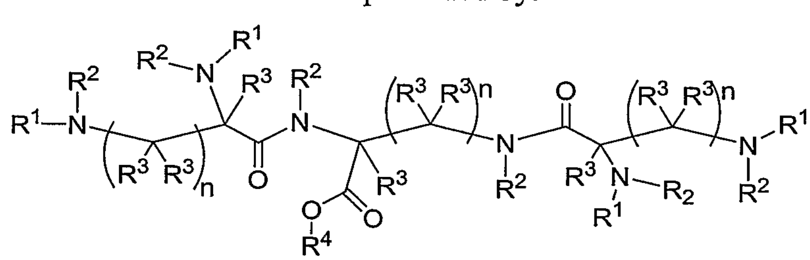
69. The method of any one of claims 37-67, wherein said patient is a human.

70. An ocular lens formed using the method of claim 37.

71. The method of claim 32 or 66, wherein said sterilizing is effective to achieve a sterility assurance level of at least about 10^{-3}.

72. The method of claim 32 or 66, wherein said sterilizing is effective to achieve a sterility assurance level of at least about 10^{-6}.

73. A polymeric composition formed by exposing a dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X** to a polymerization agent sufficient to polymerize said dendrimeric compound, wherein said polymerization agent is an oxidizing agent or a compound of formula **XI**, and wherein formula **VII** is represented by:

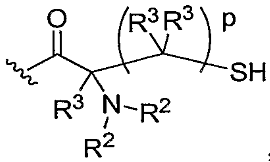
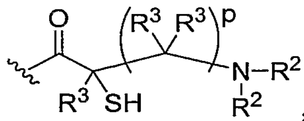
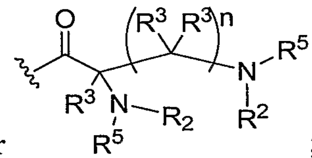


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

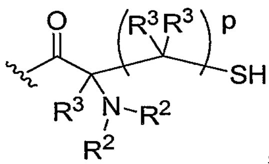
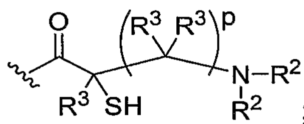
, , or ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

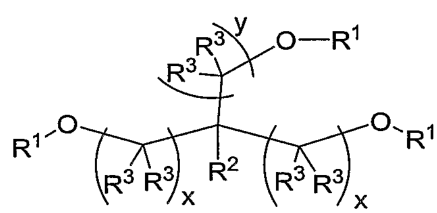
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

, or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

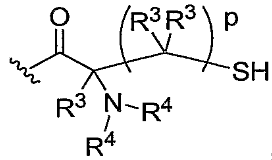
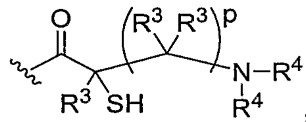
formula **VIII** is represented by:

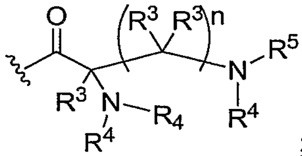


VIII

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or

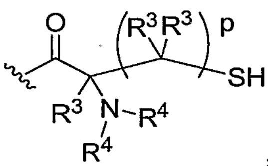
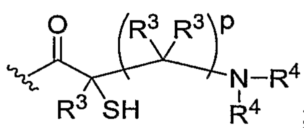
 ;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

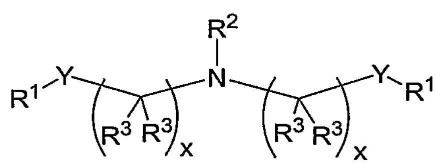
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

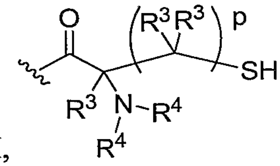
y is 0, 1, 2, 3, or 4;

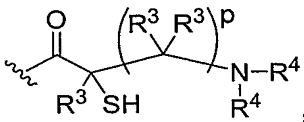
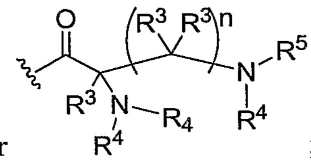
formula **IX** is represented by:

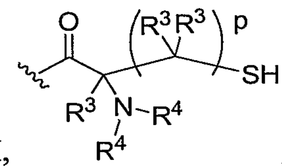
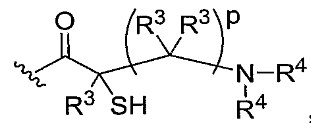


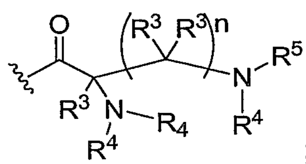
IX

wherein

R^1 represents independently for each occurrence H, -$(C(R^3)_2)_mSH$, -$C(O)(C(R^3)_2)_mSH$, -$CO_2(C(R^3)_2)_mSH$, -$C(O)N(R^2)(C(R^3)_2)_mSH$, ,

, or ;

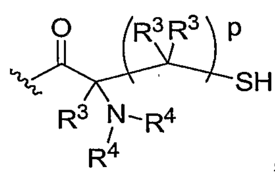
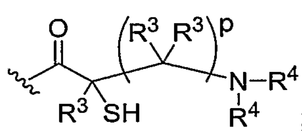
R^2 represents independently for each occurrence H, alkyl, -$(C(R^3)_2)_mYR^1$, OH, -$(C(R^3)_2)_mN(H)R^4$, -$(C(R^3)_2)_mN(R^4)OH$, -$(C(R^3)_2)_mSH$, -$C(O)(C(R^3)_2)_mSH$, -$CO_2(C(R^3)_2)_mSH$, -$C(O)N(R^2)(C(R^3)_2)_mSH$, , , or

;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, -$(C(R^3)_2)_mN(R^2)OH$, -$(C(R^3)_2)_mSH$, -$C(O)(C(R^3)_2)_mSH$, -$CO_2(C(R^3)_2)_mSH$, -$C(O)N(R^2)(C(R^3)_2)_mSH$,

, or ;

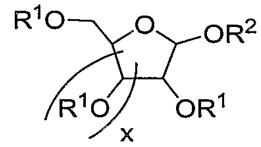
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

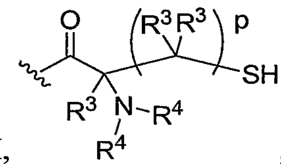
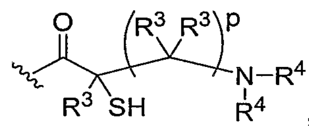
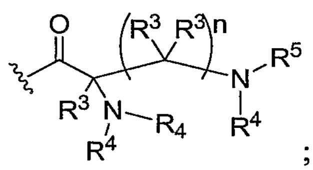
x represents independently for each occurrence 1, 2, 3, or 4;

formula **X** is represented by:



X

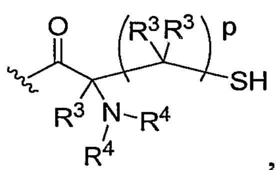
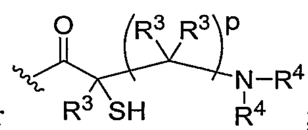
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2; and

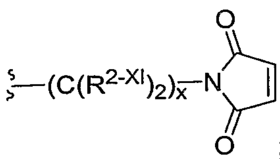
formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

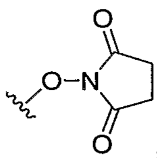
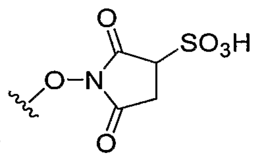
XI

wherein

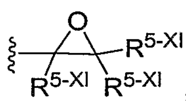
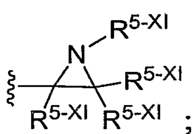
$R^{1\text{-}XI}$ represents independently for each occurrence $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yR^{4\text{-}XI}$, or

 ;

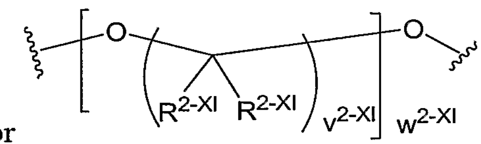
$R^{2\text{-}XI}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}XI}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, -CH_2NO_2,  , or  ;

$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S,

 , or  ;

$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or  ;

$v^{2\text{-}XI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}XI}$ is an integer in the range of about 5 to 700, inclusive; and

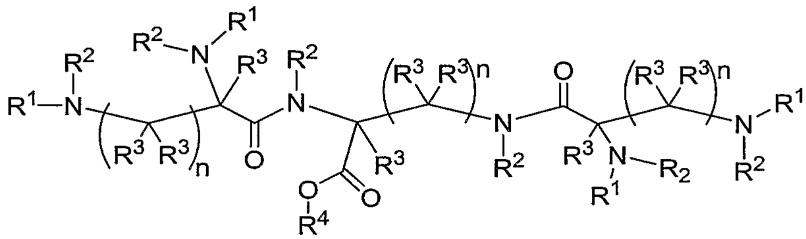
x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

74. A polymeric composition represented by formula **XIII**:

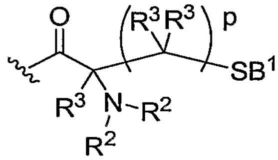
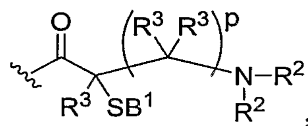
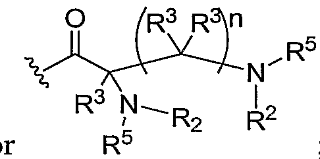
$$A^1\left[L^1-A^2\left[L^2-A^3\right]_d\right]_e$$

XIII

wherein

A^1 is  or a pharmaceutically acceptable salt, solvate, or hydrate thereof;

R^1 represents independently for each occurrence H, $-OB^1$, $-(C(R^3)_2)_mN(R^2)OB^1$, $-(C(R^3)_2)_mSB^1$, $-C(O)(C(R^3)_2)_mSB^1$, $-CO_2(C(R^3)_2)_mSB^1$, $-C(O)N(R^2)(C(R^3)_2)_mSB^1$,

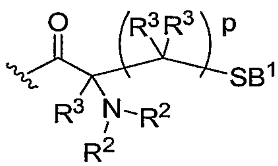
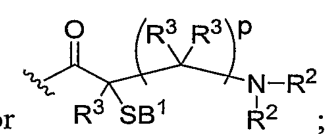
 ,  , or  ;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence $-OB^1$, $-(C(R^3)_2)_mN(R^2)OB^1$, $-(C(R^3)_2)_mSB^1$, $-C(O)(C(R^3)_2)_mSB^1$, $-CO_2(C(R^3)_2)_mSB^1$, $-C(O)N(R^2)(C(R^3)_2)_mSB^1$,

 , or  ;

B^1 represents independently for each occurrence H or a bond to L^1;

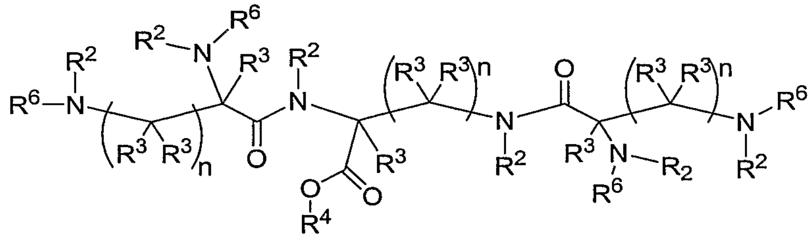
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

d represents independently for each occurrence 0, 1, or 2;

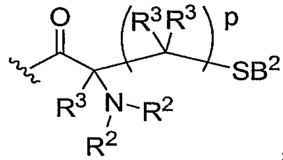
e is 1, 2, 3, or 4;

A^2 represents independently for each occurrence



or a pharmaceutically acceptable salt, solvate, or hydrate thereof;

R^6 represents independently for each occurrence H, $-OB^2$, $-(C(R^3)_2)_mN(R^2)OB^2$, $-(C(R^3)_2)_mSB^2$, $-C(O)(C(R^3)_2)_mSB^2$, $-CO_2(C(R^3)_2)_mSB^2$, $-C(O)N(R^2)(C(R^3)_2)_mSB^2$,



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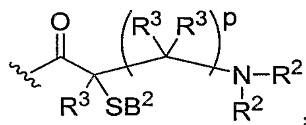
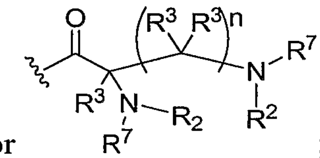
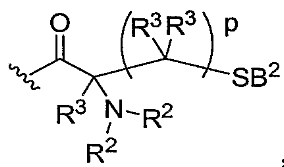


, or

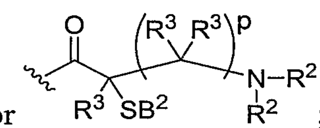


;

R^7 represents independently for each occurrence $-OB^2$, $-(C(R^3)_2)_mN(R^2)OB^2$, $-(C(R^3)_2)_mSB^2$, $-C(O)(C(R^3)_2)_mSB^2$, $-CO_2(C(R^3)_2)_mSB^2$, $-C(O)N(R^2)(C(R^3)_2)_mSB^2$,



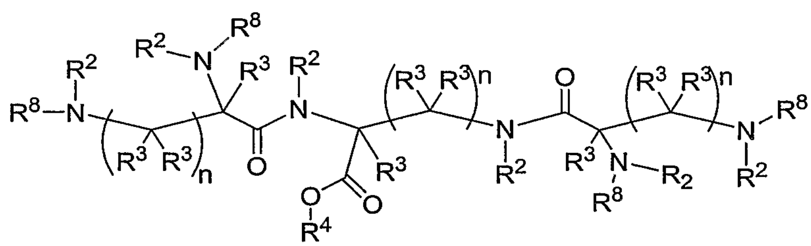
, or



;

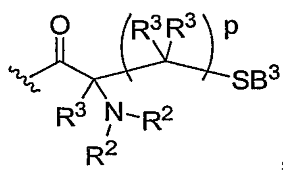
B^2 represents independently for each occurrence H, a bond to L^1, or a bond to L^2;

A^3 represents independently for each occurrence



or a pharmaceutically acceptable salt, solvate, or hydrate thereof;

R^8 represents independently for each occurrence H, $-OB^3$, $-(C(R^3)_2)_mN(R^2)OB^3$, $-(C(R^3)_2)_mSB^3$, $-C(O)(C(R^3)_2)_mSB^3$, $-CO_2(C(R^3)_2)_mSB^3$, $-C(O)N(R^2)(C(R^3)_2)_mSB^3$,



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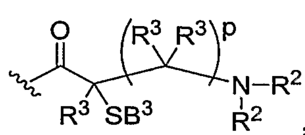
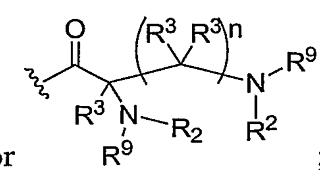
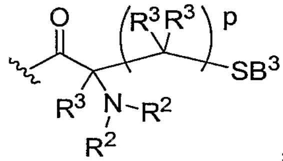


, or



;

R^9 represents independently for each occurrence $-OB^3$, $-(C(R^3)_2)_mN(R^2)OB^3$, $-(C(R^3)_2)_mSB^3$, $-C(O)(C(R^3)_2)_mSB^3$, $-CO_2(C(R^3)_2)_mSB^3$, $-C(O)N(R^2)(C(R^3)_2)_mSB^3$,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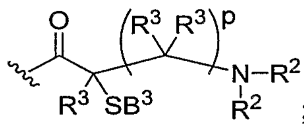
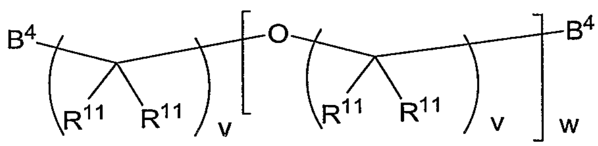

;

B^3 represents independently for each occurrence H or a bond to L^2;

L^1 represents independently for each occurrence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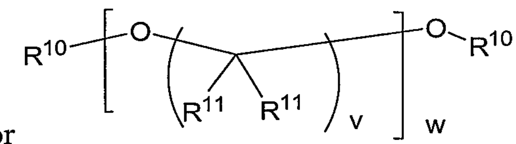
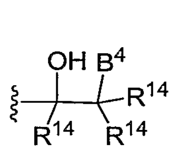
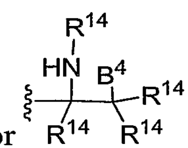

;

R^{10} represents independently for each occurrence $-(C(R^{11})_2)_xC(O)B^4$, $-(C(R^{11})_2)_xR^{12}$, $-C(O)(C(R^{11})_2)_yC(O)B^4$, $-C(O)(C(R^{11})_2)_yR^{12}$, $-(C(R^{11})_2)_xR^{13}$, or $-C(O)(C(R^{11})_2)_yR^{13}$;

R^{11} represents independently for each occurrence H, alkyl, or halogen;

R^{12} represents independently for each occurrence $-C(OH)(alkyl)B^4$, $-C(OH)(fluoroalkyl)B^4$, $-C(OH)(chloroalkyl)B^4$, or $-C(OH)(CH_2NO_2)B^4$;

R^{13} represents independently for each occurrence $-N(H)C(O)B^4$, $-N(H)C(S)B^4$,


, or

;

R^{14} represents independently for each occurrence H, alkyl, or aralkyl;

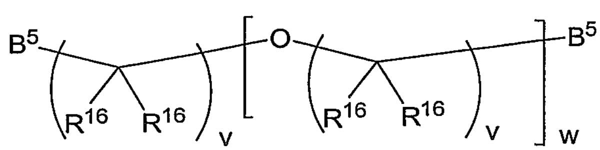
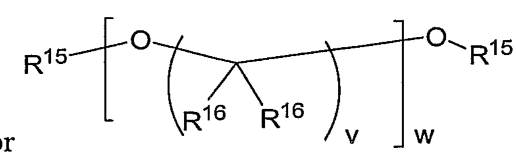
B^4 represents independently for each occurrence a bond to A^1 or A^2;

v represents independently for each occurrence 2, 3, or 4;

w is an integer in the range of about 5 to 7000, inclusive;

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9;

L^2 represents independently for each occurrence

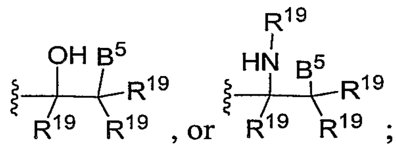

or

;

R^{15} represents independently for each occurrence $-(C(R^{16})_2)_xC(O)B^5$, $-(C(R^{16})_2)_xR^{17}$, $-C(O)(C(R^{16})_2)_yC(O)B^5$, $-C(O)(C(R^{16})_2)_yR^{17}$, $-(C(R^{16})_2)_xR^{18}$, or $-C(O)(C(R^{16})_2)_yR^{18}$;

R^{16} represents independently for each occurrence H, alkyl, or halogen;

R^{17} represents independently for each occurrence $-C(OH)(alkyl)B^5$, $-C(OH)(fluoroalkyl)B^5$, $-C(OH)(chloroalkyl)B^5$, or $-C(OH)(CH_2NO_2)B^5$;

R^{18} represents independently for each occurrence $-N(H)C(O)B^5$, $-N(H)C(S)B^5$,

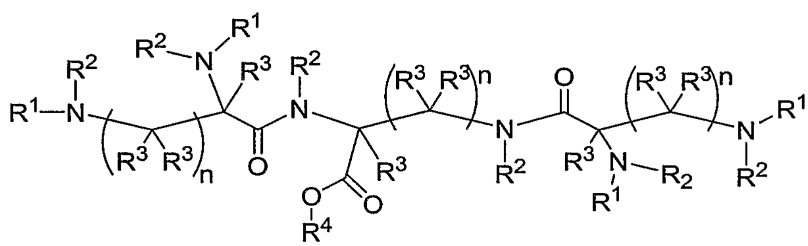


R^{19} represents independently for each occurrence H, alkyl, or aralkyl; and

B^5 represents independently for each occurrence a bond to A^2 or A^3.

75. A pharmaceutical composition comprising the polymeric composition of claim 74 and a pharmaceutical agent.

76. A kit for the preparation of a sealant comprising a polymerizable dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X**, and instructions for preparing said sealant; wherein formula **VII** is represented by:

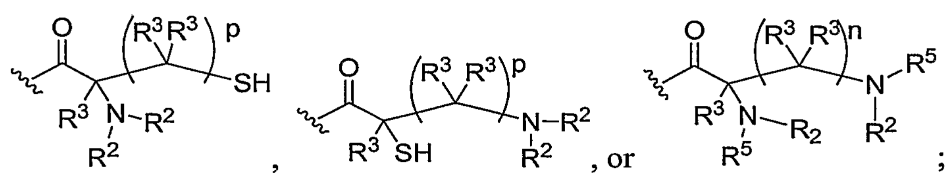


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

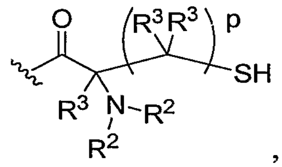
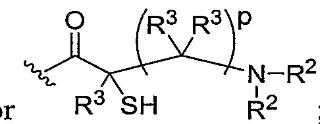


R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

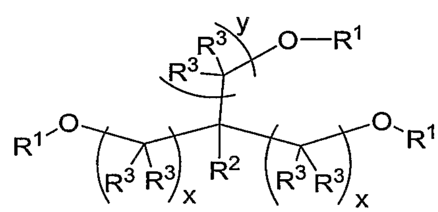
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,


, or

;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

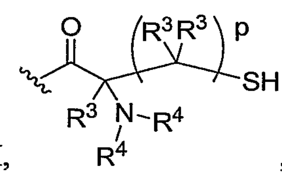
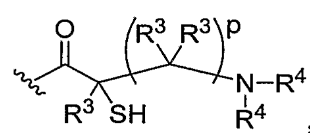
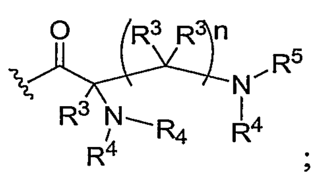
formula **VIII** is represented by:



VIII

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

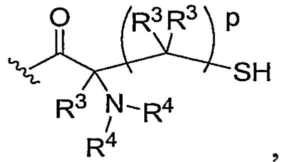
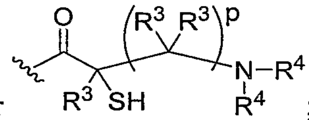

,

, or

;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

, or  ;

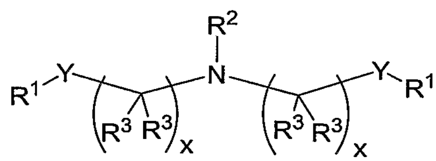
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

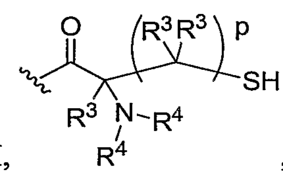
y is 0, 1, 2, 3, or 4;

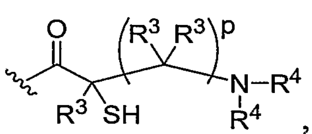
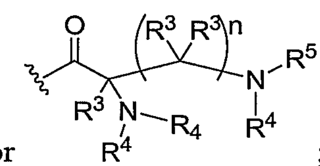
formula **IX** is represented by:



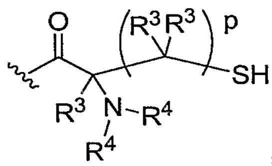
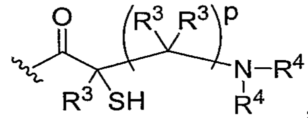
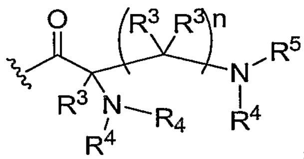
IX

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, ,

, or  ;

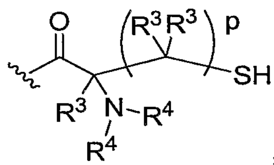
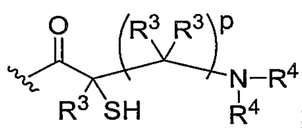
R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, -

$CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or  ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

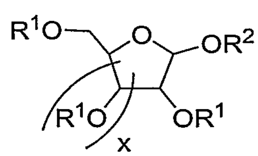
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x represents independently for each occurrence 1, 2, 3, or 4;

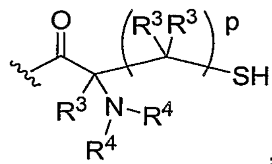
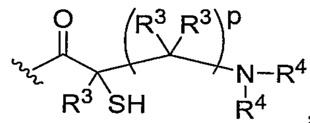
formula **X** is represented by:

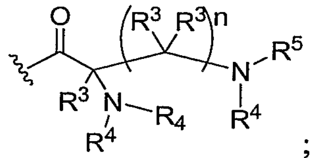


X

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or

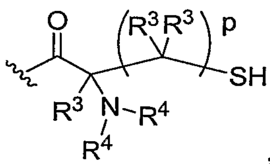
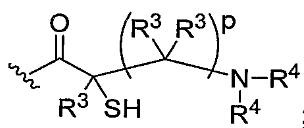
 ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2.

77. The kit of claim 76, further comprising a desiccant.

78. The kit of claim 76, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

79. The kit of claim 76, further comprising a polymerization agent.

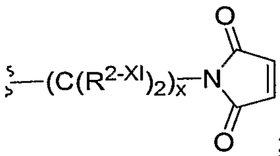
80. The kit of claim 79, wherein said polymerization agent is a compound of formula **XI**; wherein formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

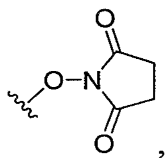
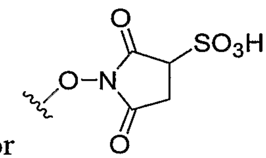
XI

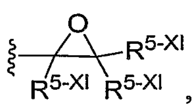
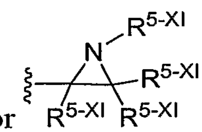
wherein

$R^{1\text{-}XI}$ represents independently for each occurrence $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yR^{4\text{-}XI}$, or

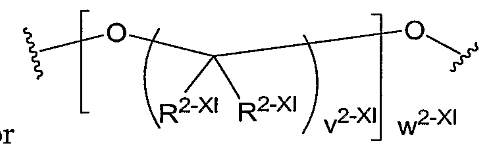

;

$R^{2\text{-}XI}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}XI}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, $-CH_2NO_2$,  , or  ;

$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S,  , or  ;

$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

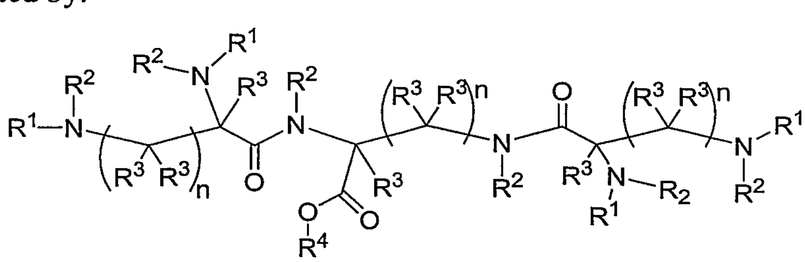
B is alkyl diradical, heteroalkyl diradical, or  ;

$v^{2\text{-}XI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}XI}$ is an integer in the range of about 5 to 700, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

81. A kit for the preparation of a lens comprising a polymerizable dendrimeric compound of formulae **VII**, **VIII**, **IX**, or **X**, and instructions for preparing said lens; wherein formula **VII** is represented by:

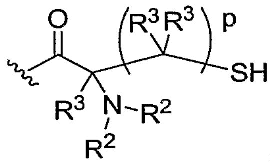
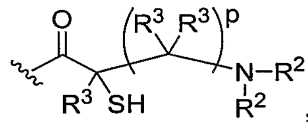
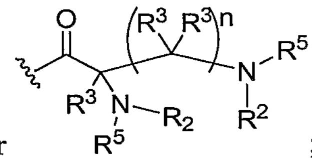


VII

or a pharmaceutically acceptable salt, solvate, or hydrate thereof,

wherein

R^1 represents independently for each occurrence H, OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

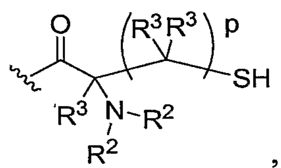
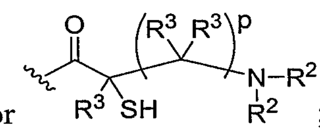

,

, or

;

R^2 represents independently for each occurrence H or alkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence alkyl, aryl, or aralkyl;

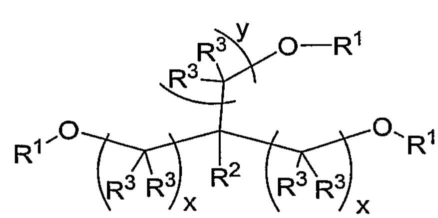
R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,


, or

;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

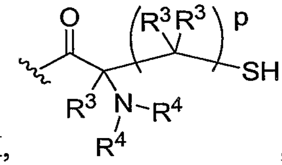
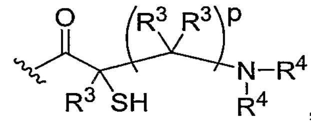
formula **VIII** is represented by:

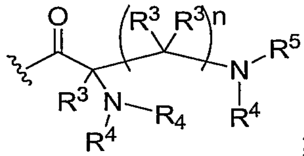


VIII

wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, -

$C(O)N(R^2)(C(R^3)_2)_mSH$,  ,  , or

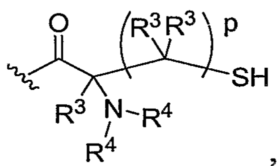
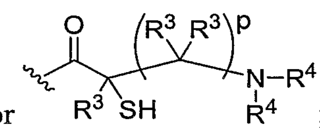
 ;

R^2 represents independently for each occurrence H, alkyl, or $-(C(R^3)_2)_xOR^1$;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$,

 , or  ;

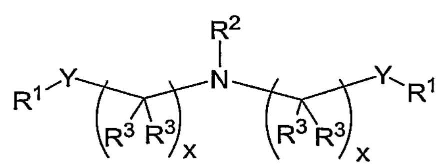
n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5;

x represents independently for each occurrence 1, 2, 3, or 4; and

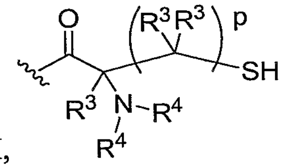
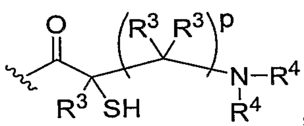
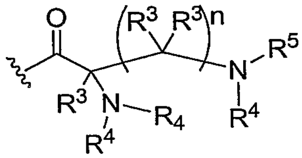
y is 0, 1, 2, 3, or 4;

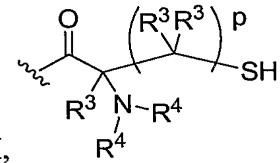
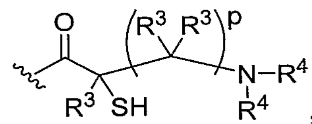
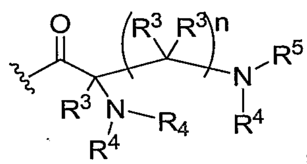
formula **IX** is represented by:



IX

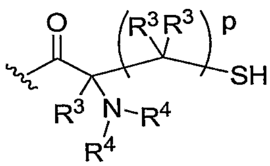
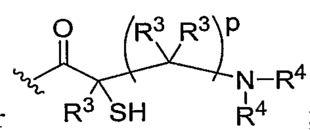
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence H, alkyl, $-(C(R^3)_2)_mYR^1$, OH, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^2)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

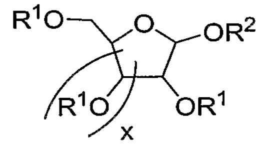
Y represent independently for each occurrence O or NR^4;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

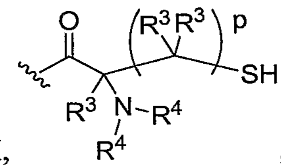
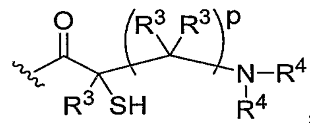
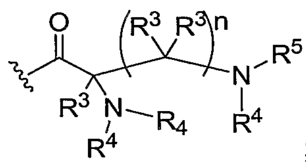
x represents independently for each occurrence 1, 2, 3, or 4;

formula **X** is represented by:



X

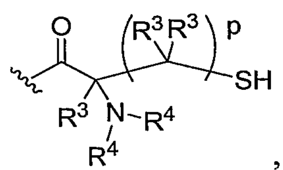
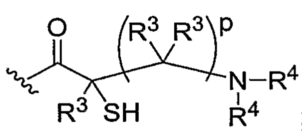
wherein

R^1 represents independently for each occurrence H, $-(C(R^3)_2)_mN(H)R^4$, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , , or ;

R^2 represents independently for each occurrence alkyl, aryl, or aralkyl;

R^3 represents independently for each occurrence H, halogen, or alkyl;

R^4 represents independently for each occurrence H, alkyl, aryl, or aralkyl;

R^5 represents independently for each occurrence OH, $-(C(R^3)_2)_mN(R^4)OH$, $-(C(R^3)_2)_mSH$, $-C(O)(C(R^3)_2)_mSH$, $-CO_2(C(R^3)_2)_mSH$, $-C(O)N(R^2)(C(R^3)_2)_mSH$, , or ;

n and m each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, or 8;

p represents independently for each occurrence 1, 2, 3, 4, or 5; and

x is 1 or 2.

82. The kit of claim 81, further comprising a desiccant.

83. The kit of claim 81, further comprising an inert atmosphere to prevent reaction of said dendrimeric compound with atmospheric molecules.

84. The kit of claim 81, further comprising a polymerization agent.

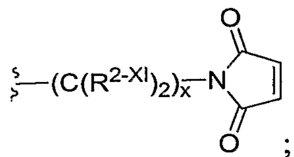
85. The kit of claim 84, wherein said polymerization agent is a compound of formula **XI**; wherein formula **XI** is represented by:

$$R^{1\text{-}XI}—B—R^{1\text{-}XI}$$

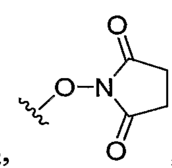
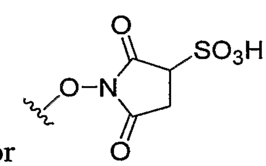
XI

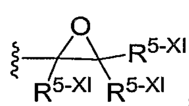
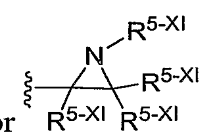
wherein

$R^{1\text{-}XI}$ represents independently for each occurrence $-(C(R^{2\text{-}XI})_2)_xC(O)R^{3\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yC(O)R^{3\text{-}XI}$, $-(C(R^{2\text{-}XI})_2)_xR^{4\text{-}XI}$, $-C(O)(C(R^{2\text{-}XI})_2)_yR^{4\text{-}XI}$, or

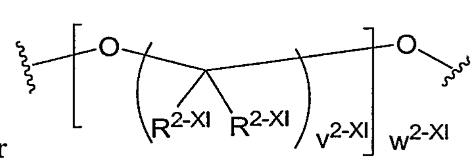

;

$R^{2\text{-}XI}$ represents independently for each occurrence H, alkyl, or halogen;

$R^{3\text{-}XI}$ represents independently for each occurrence alkyl, fluoroalkyl, chloroalkyl, $-CH_2NO_2$, , or  ;

$R^{4\text{-}XI}$ represents independently for each occurrence -N=C=O, -N=C=S, , or  ;

$R^{5\text{-}XI}$ represents independently for each occurrence H, alkyl, or aralkyl;

B is alkyl diradical, heteroalkyl diradical, or  ;

$v^{2\text{-}XI}$ represents independently for each occurrence 2, 3, or 4;

$w^{2\text{-}XI}$ is an integer in the range of about 5 to 7000, inclusive; and

x and y each represent independently for each occurrence 1, 2, 3, 4, 5, 6, 7, 8, or 9.

86. The kit of claim 76 or 81, wherein said kit has a sterility assurance level of at least about 10^{-3}.

87. The kit of claim 76 or 81, wherein said kit has a sterility assurance level of at least about 10^{-6}.

Figure 1

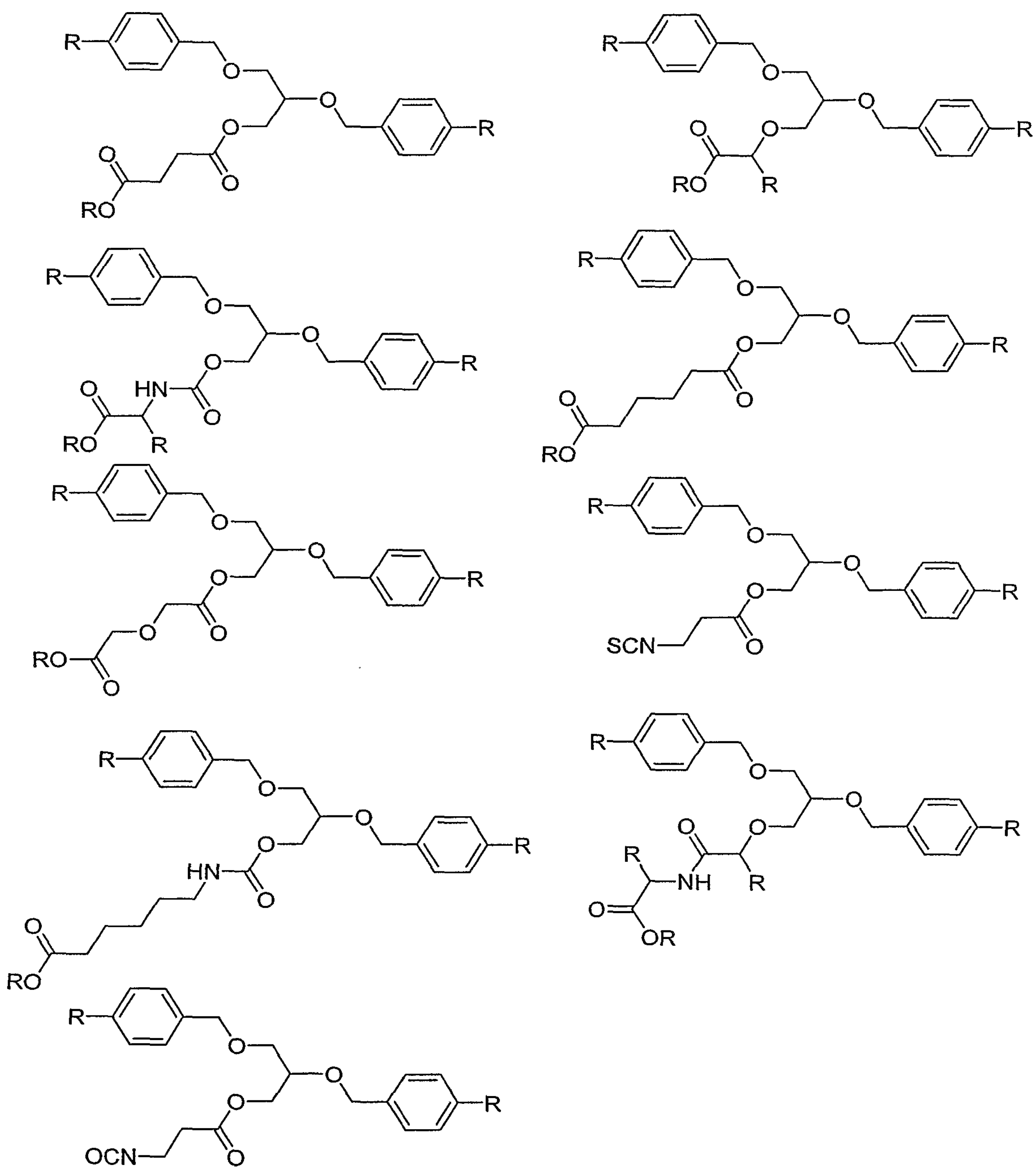


Figure 2

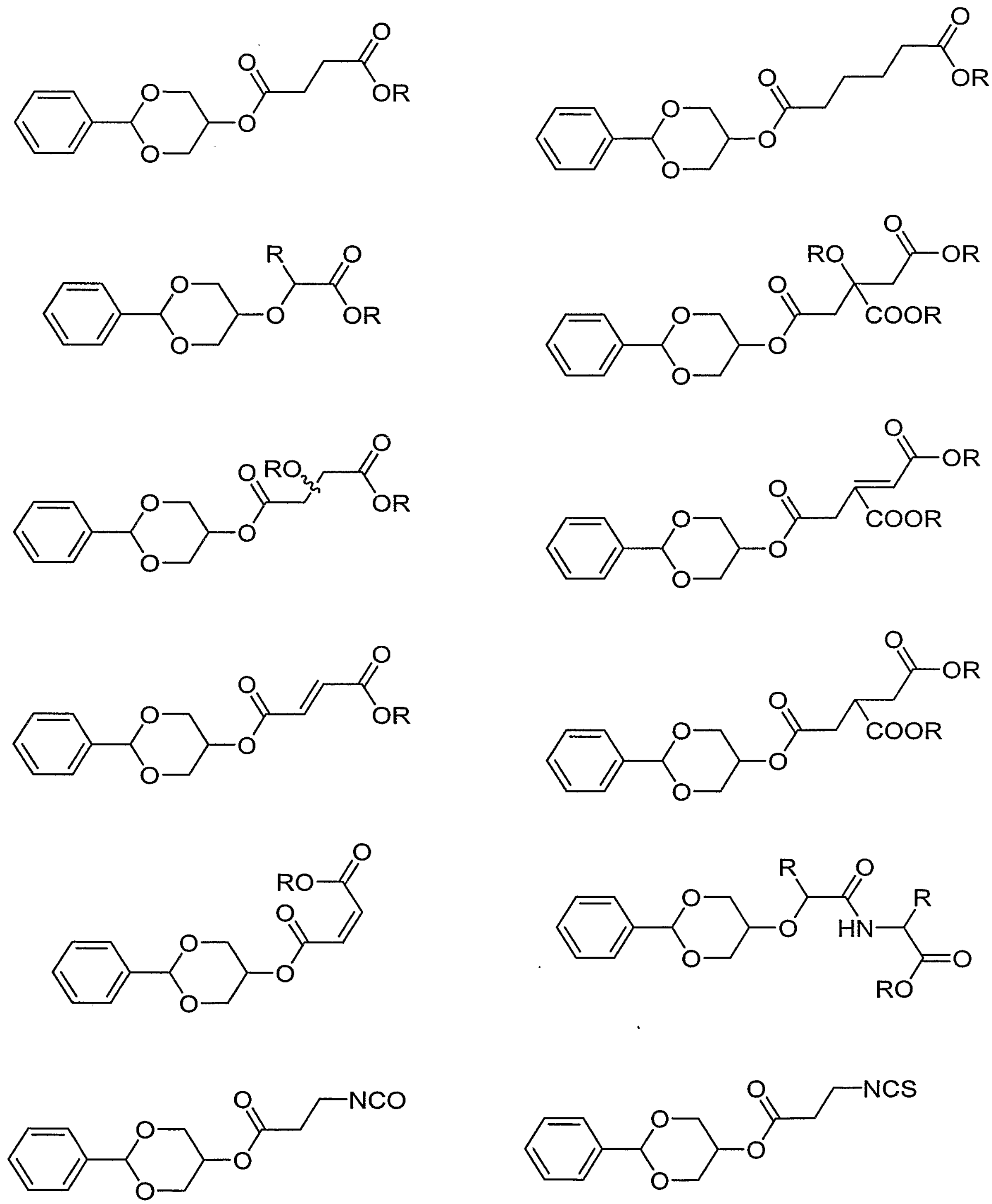


Figure 3

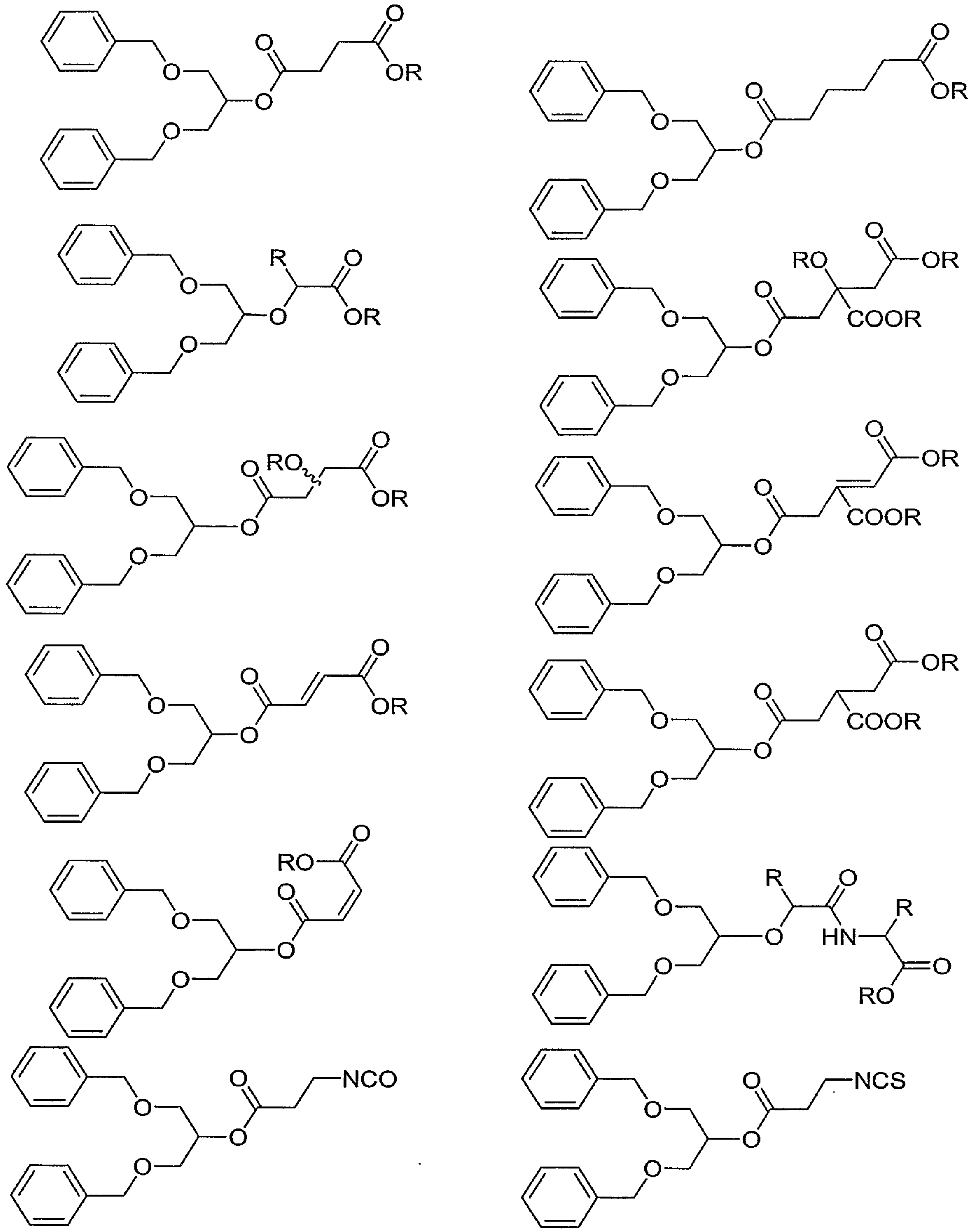


Figure 4

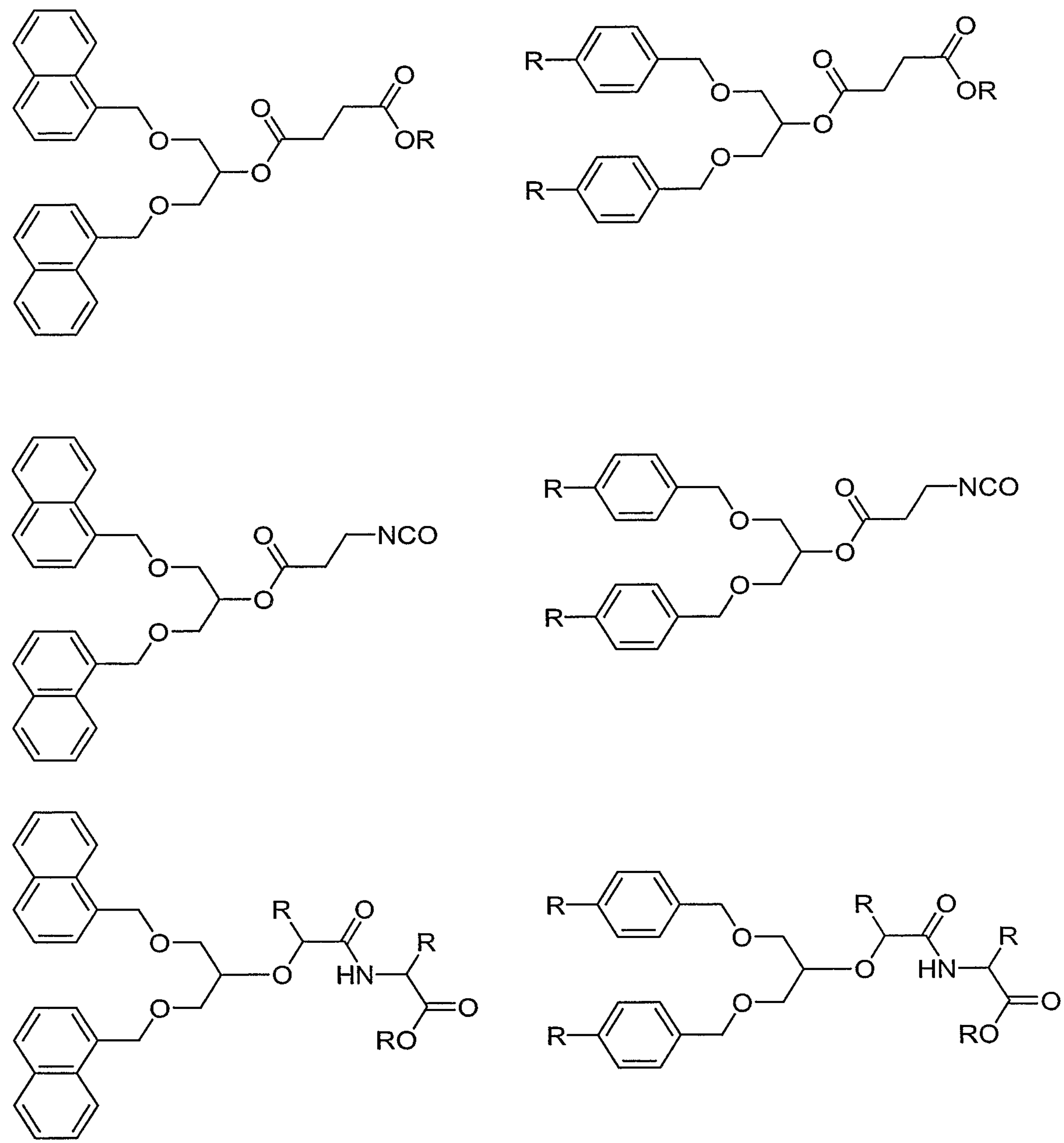


Figure 5

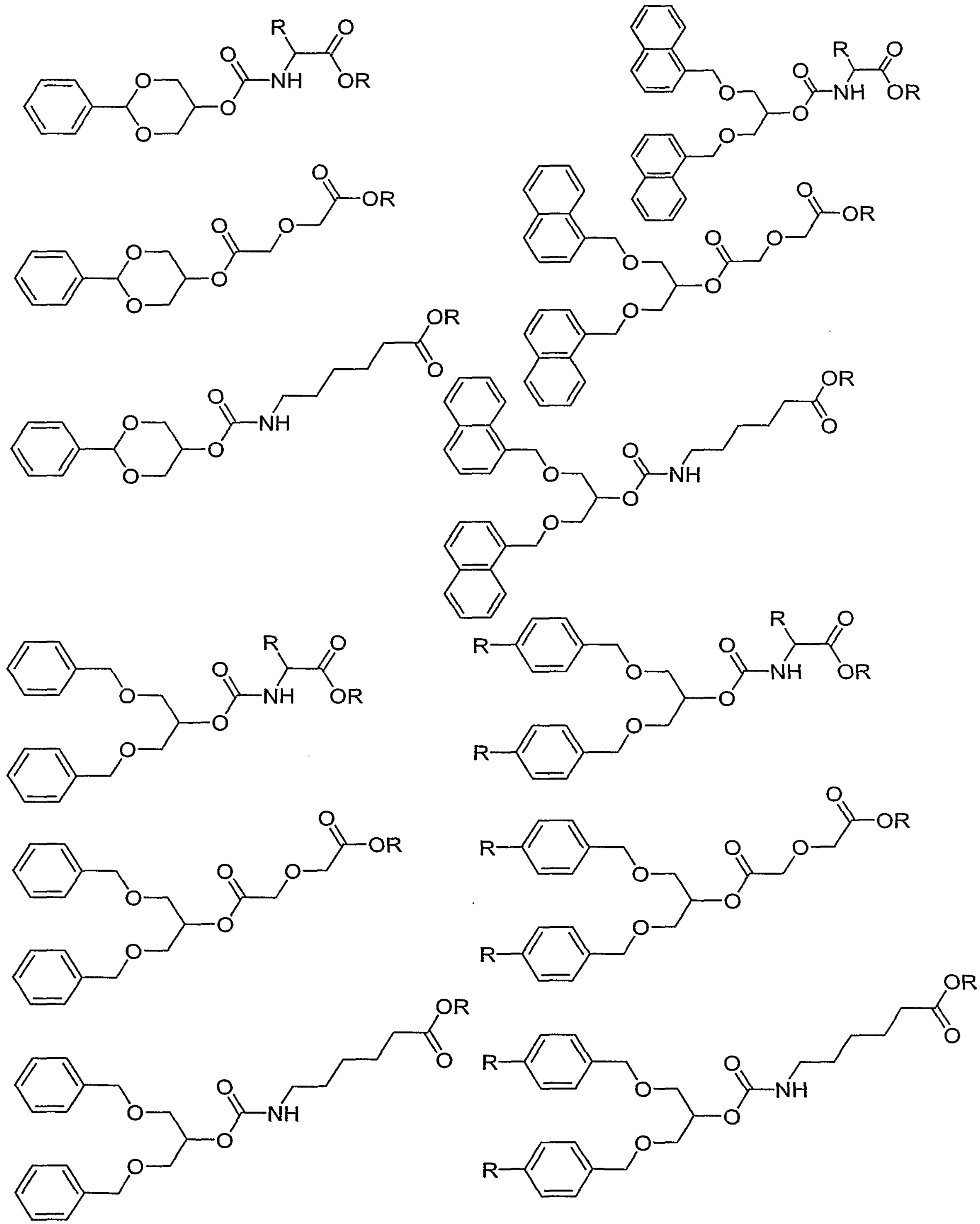


Figure 6

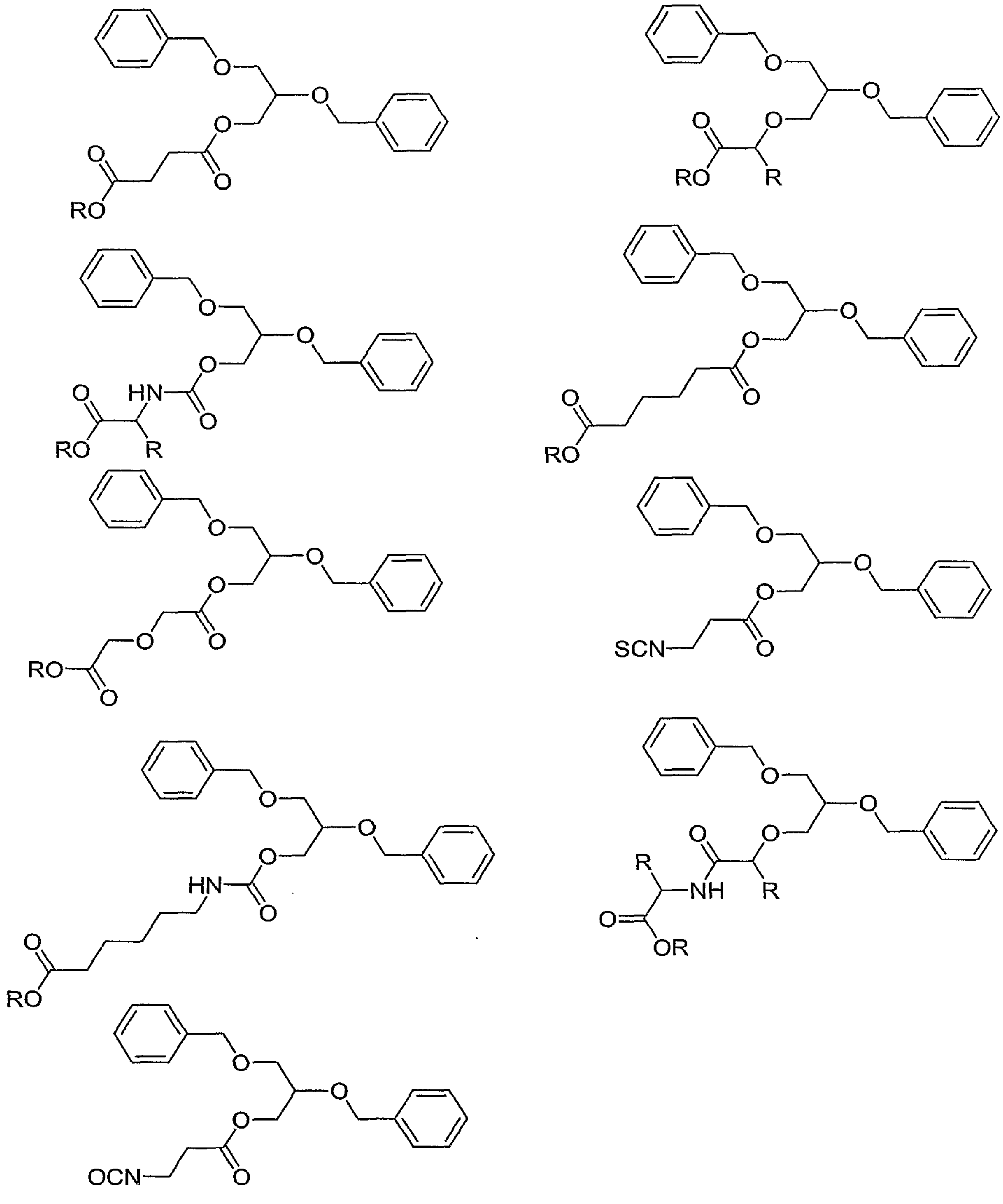


Figure 7

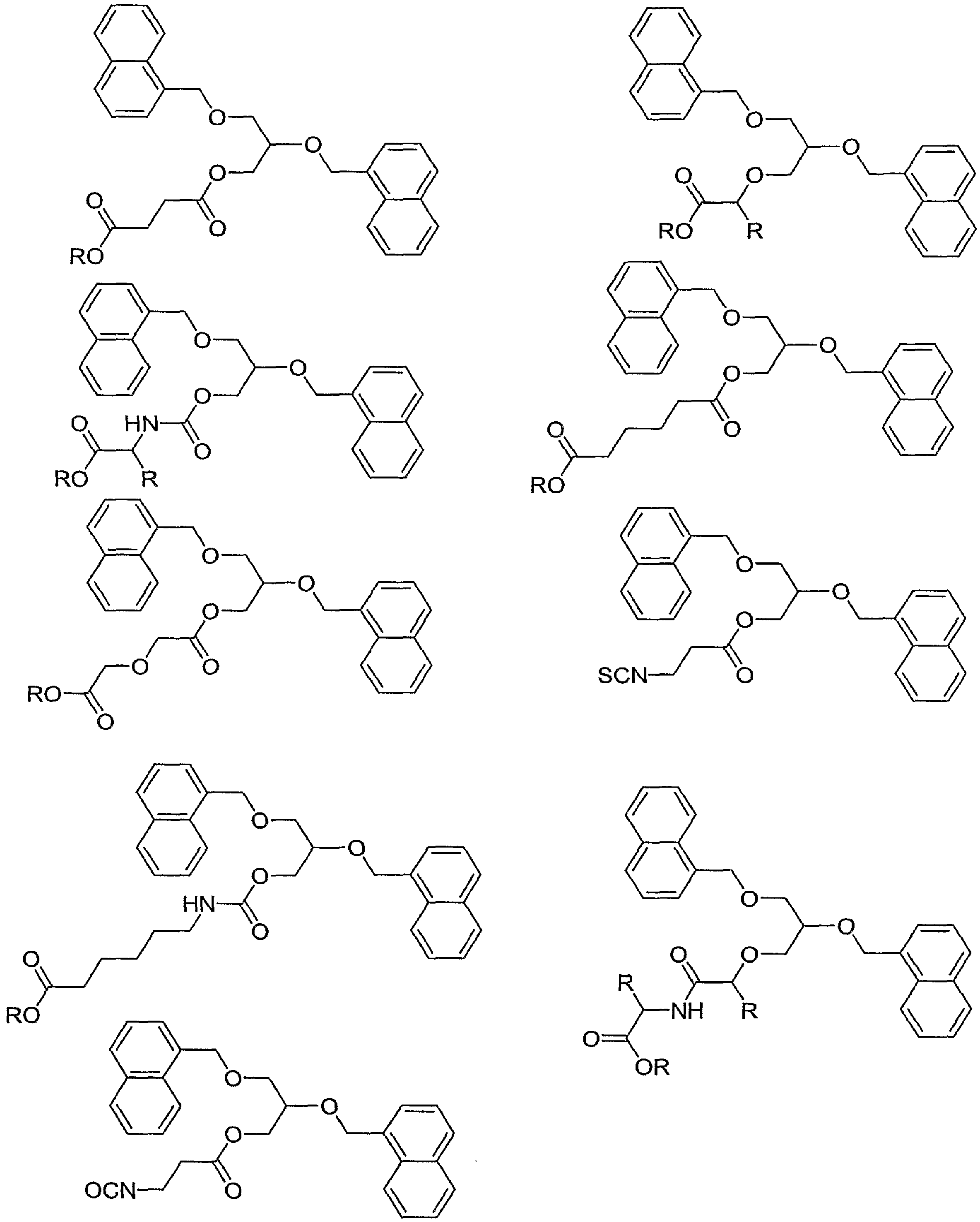


Figure 8

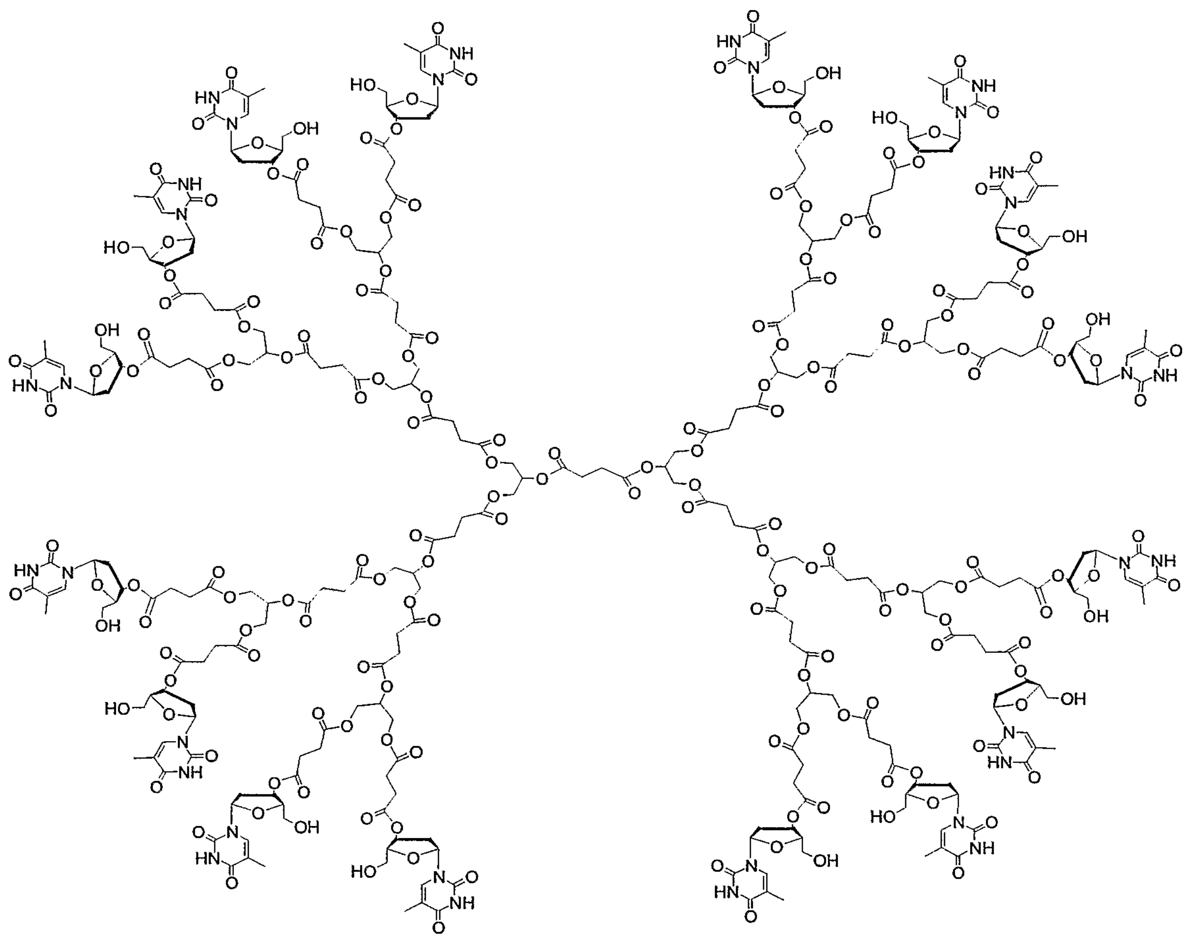
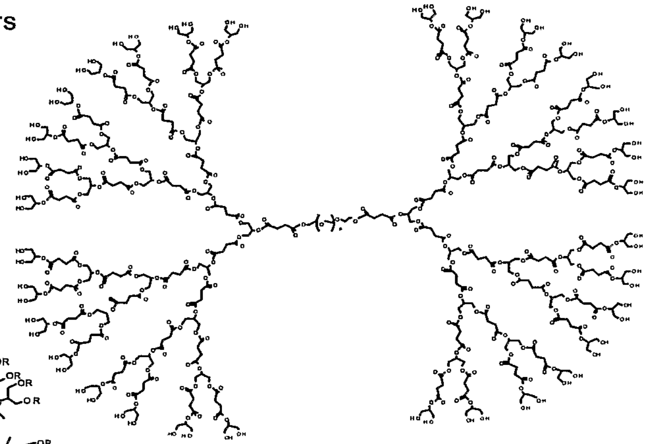
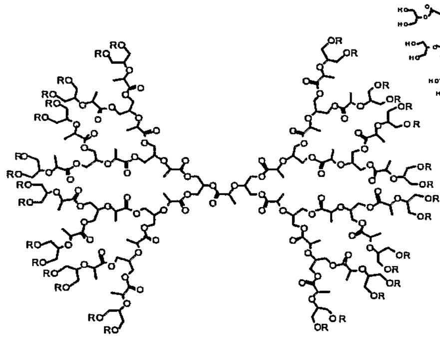


Figure 9

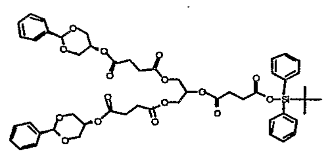
Examples of dendritic polymers



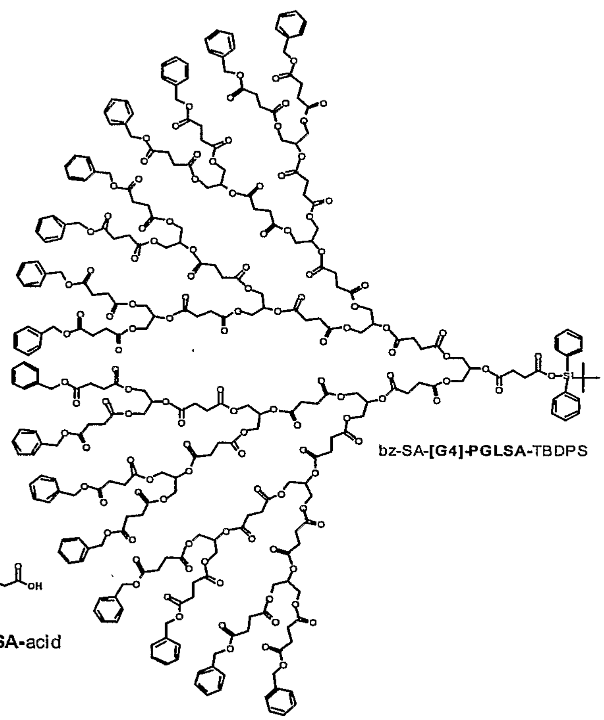
([G4]-PGLSA-OH)$_2$-PEG (3400 Mw)



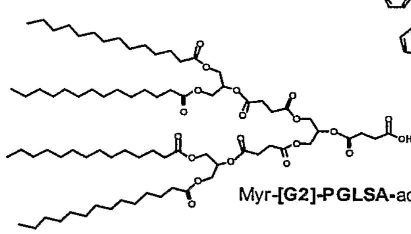
R = H [G3]-PGLLA-OH



bzld-[G2]-PGLSA-TBDPS



bz-SA-[G4]-PGLSA-TBDPS



Myr-[G2]-PGLSA-acid

Figure 10

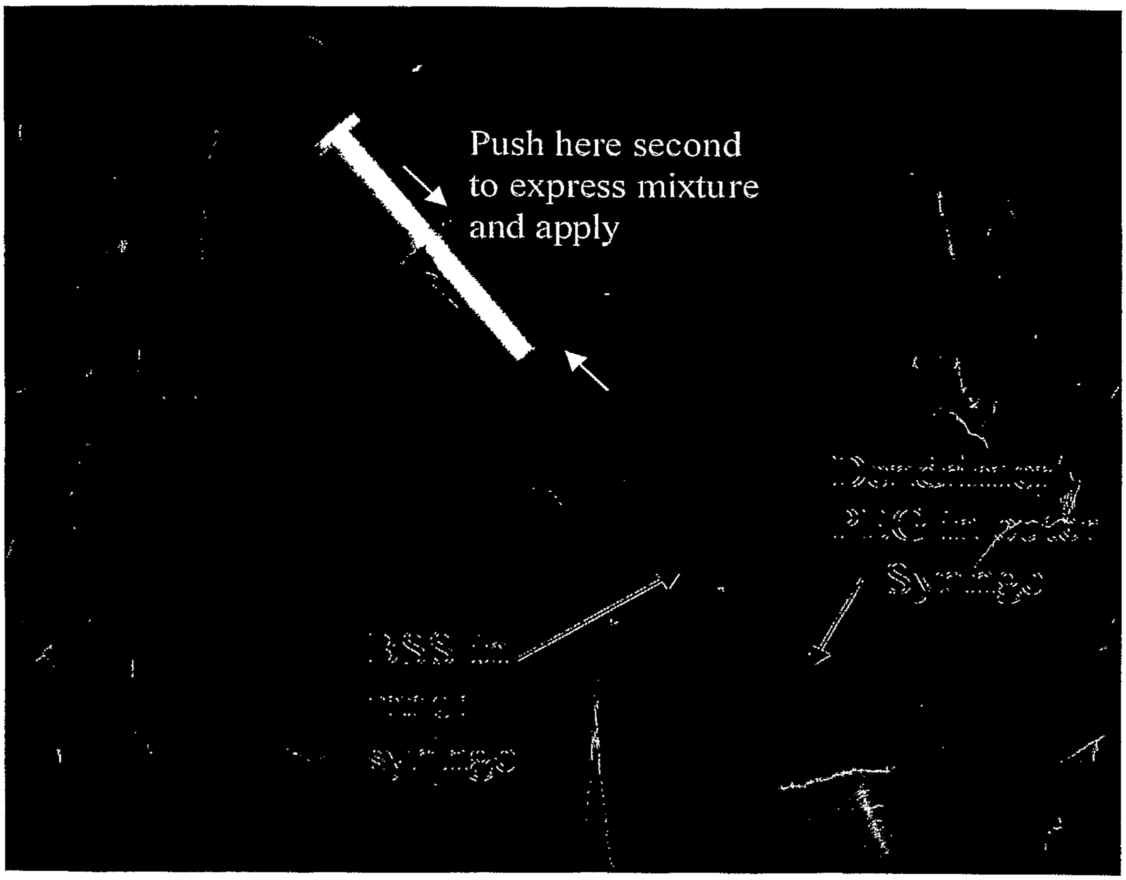


Figure 11